

# **CalTOX Version 2.3**

## **Description of Modifications and Revisions**

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**FORWARD**

The Department of Toxic Substances Control (DTSC), within the California Environmental Protection Agency, has the responsibility for managing the State's hazardous-waste program to protect public health and the environment. The Human and Ecological Risk Division (HERD) within the DTSC provides scientific assistance in the areas of toxicology, risk, environmental assessment, training, and guidance to the regional offices within DTSC. Part of this assistance and guidance is the preparation of regulations, scientific standards, guidance documents, and recommended procedures for use by regional staff, local governmental agencies, or responsible parties and their contractors in the characterization and mitigation of hazardous-waste-substances-release sites. The CalTOX model has been developed as a compiled spreadsheet model to assist in exposure and health-risk assessments that address contaminated soils and the contamination of adjacent air, surface water, sediments, and ground water. CalTOX has been developed under the auspices of the University of California with funding provided by the DTSC. The development effort has involved the Ernest Orlando Lawrence Berkeley National Laboratory (The Berkeley Lab) and the Lawrence Livermore National Laboratory (LLNL) and has involved the Berkeley (UCB), Davis (UCD), and Los Angeles (UCLA) campuses of the University. The modeling components of CalTOX include multimedia transport and transformation models, exposure scenario models, and efforts to quantify and reduce uncertainty in multimedia, multiple-pathway exposure models. This report describes a number of modifications that were made to the CalTOX model in order to address some of the limitations that were identified in the early version of the model. These modifications were carried out primarily to make CalTOX applicable to assessing the health risks of residents living near landfills containing toxic chemicals.

INTRODUCTION.....1

BACKGROUND ON THE SCOPE OF WORK.....2

    Linking Multimedia Concentrations to Total Human Exposure .....3

    The Multimedia Transport and Transformation Model .....3

    Balancing Gains and Losses—Sources, Transport, and Transformation .....5

REVISIONS TO THE MULTIMEDIA MASS-BALANCE EQUATIONS.....6

    Including Both Batch and Continuous Inputs to the Root-Zone Soil .....6

    Average Compartment Inventories Over the Exposure Duration .....6

    The Revision of CalTOX Gain-Loss Equations .....7

MODIFICATIONS TO SOIL/PLANT MODELING IN CALTOX ..... 11

    The Revised Air/Soil/Plant Model ..... 11

    Changes to Fugacity Capacities ..... 12

        Fugacity capacity of the root-soil compartment,  $Z_s$  ..... 13

        Fugacity capacity of plant roots,  $Z_{pr}$  ..... 13

        Fugacity capacity of above-ground plant biomass ..... 14

        Fugacity capacity of phloem liquid,  $Z_{phl}$  ..... 14

    Changes to Plant Mass Transfer Rate Constants ..... 15

        Between air and plants,  $T_{ap}$ ,  $T_{pa}$ ..... 15

        Between ground-surface soil and plants,  $T_{gp}$ ,  $T_{pg}$  ..... 16

        Between root-zone soil and plants,  $T_{sp}$ ,  $T_{ps}$ ..... 17

SOIL CONCENTRATIONS THAT EXCEED THE FUGACITY-CAPACITY LIMIT

    AS NON-AQUEOUS-PHASE MASS(NAPM)..... 18

        Root-Zone Soil Compartment..... 19

        Vadose-Zone Soil Compartment..... 21

OFF-SITE TRANSFERS IN AIR AND GROUND WATER..... 22

    Contamination of Adjacent Landscape Media by Air Transport Off Site ..... 25

        Atmospheric dispersion modeling ..... 25

        On-site concentration and effective source term ..... 26

        Determining off-site concentrations ..... 28

        Calculating off-site surface-media fugacities and concentrations ..... 31

    Contamination of Off-Site Ground Water ..... 32

        Mathematical development..... 32

        On-site ground water concentration and the penetration depth,  $Z$  ..... 36

SUMMARY AND DISCUSSION..... 38

REFERENCES..... 40

## INTRODUCTION

CalTOX has been developed as a set of spreadsheet models and spreadsheet data sets to assist in assessing human exposures and defining soil clean-up levels at uncontrolled hazardous waste sites. CalTOX addresses contaminated soils and the contamination of adjacent air, surface water, sediments, and ground water. The modeling components of CalTOX include a multimedia transport and transformation model, exposure scenario models, and efforts to quantify and reduce uncertainty in those models.

The multimedia transport and transformation model is a dynamic model that can be used to assess time-varying concentrations of contaminants introduced initially to soil layers or for contaminants released continuously to air or water. This model assists the user in examining how chemical and landscape properties impact both the ultimate route and quantity of human contact. Using this model, we view the environment as a series of interacting compartments. The model allows the user to determine whether a substance will (a) remain or accumulate within the compartment of its origin, (b) be physically, chemically, or biologically transformed within the compartment of its origin (i.e., by hydrolysis, oxidation, etc.), or (c) be transported to another compartment by cross-media transfer that involves dispersion or advection (i.e., volatilization, precipitation, etc.).

Multimedia, multiple pathway exposure models are used in CalTOX to estimate average daily doses within a human population in the vicinity of a hazardous substances release site. The exposure models encompass twenty-three exposure pathways. The exposure assessment process consists of relating contaminant concentrations in the multimedia model compartments to contaminant concentrations in the media with which a human population has contact (personal air, tap water, foods, household dusts soils, etc.). The average daily dose is the product of the exposure concentrations in these contact media and an intake or uptake factor that relates the concentrations to the distributions of potential dose within the population.

This report describes a number of modifications that were made to the CalTOX model during 1995 and 1996 in order to address some of the limitations that were identified in the early version of the model. These changes include (1) redefining the CalTOX equations so that there can be both batch and continuous inputs to the root-zone soil, (2) altering the way the plants compartment interacts with soil and air, (3) allowing CalTOX to handle chemical concentrations in soil that exceed the aqueous-phase solubility limit, and (4) add to CalTOX the ability to simulate off-site transfers of contaminants through air pathways and through the subsurface environment—vapor phase-transport in the vadose zone and ground water transport. These modifications were carried out primarily to make CalTOX applicable to assessing the health risks of residents living near landfills containing toxic chemicals.

This report is divided into six sections. The first section provides some background on the evolution and development of multimedia mass-balance and exposure models in general and the development of the CalTOX model in particular. The next section describes how the CalTOX model was modified to have both batch and continuous inputs to the root-zone soil. This section also gives an overview on the current form of and solution for the CalTOX multimedia mass-balance equations. The third section describes modifications that were made to better characterize plant/air and plant/soil interactions. The next section addresses modifications that were needed to allow concentrations in root-zone soil to exceed the fugacity limit such that non-aqueous-phase mass are formed. The fifth section describes modifications that have been made to make possible the calculation of environmental media concentrations that result from transport of contaminant off site by atmospheric dispersion and to outline calculation of off-site sub-surface transport in vadose zone and in the saturated zone. The final section provides summary and discussion of these modifications.

## **BACKGROUND ON THE SCOPE OF WORK**

Efforts to assess human exposure to contaminants from multiple environmental media have been evolving over the last several decades (examples include US NRC, 1977; Bennett, 1981; US EPA 1985, 1988, 1989a, 1989b, 1992; McKone and Layton, 1986; Whicker and Kirchner, 1987; McKone & Daniels, 1991; NAS, 1991a, 1991b, 1994). In response to the need for multimedia models in environmental management, a number of multimedia transport and transformation models for organic chemicals and metal species have recently appeared. State of the art in modeling multimedia distribution of environmental contaminants and multi-pathway exposures of human populations has been established at the University of California campuses and National Laboratories through the integration of models and experiments (Allen et al., 1989; Bogen and McKone, 1988; Layton, 1993; Maddalena et al., 1995; McKone and Bogen, 1991; Ng, 1982). The result of these efforts have been incorporated in large part in the CalTOX model, which has been developed under the auspices of the University of California with funding provided by the California Environmental Protection Agency Department of Toxic Substances control (DTSC) (McKone, 1993a, 1993b, 1993c; Maddalena et al., 1995). CalTOX was designed to assess the fate and human-health impacts of contaminants in soil—including metals and persistent volatile and semi-volatile organic compounds.

The Human and Ecological Risk Division (HERD) within the DTSC provides scientific assistance in the areas of toxicology, risk and environmental assessment, training, and guidance to the regional offices within DTSC. Part of this assistance and guidance is the preparation of regulations, scientific standards, guidance documents, and recommended procedures for use by regional staff, local governmental agencies, or

responsible parties and their contractors in the characterization and mitigation of hazardous-waste-substances-release sites. The CalTOX model has been developed as spreadsheet model and spreadsheet data sets that can be integrated to assist in health-risk assessments. In its current form, CalTOX addresses contaminated soils and the contamination of adjacent air, surface water, sediments, and ground water.

### **Linking Multimedia Concentrations to Total Human Exposure**

Among the current needs of the exposure-assessment community is to provide data for linking exposure, dose, and health information in ways that improve environmental surveillance, improve predictive models, and enhance risk assessment and risk management (NAS, 1994). CalTOX is a dynamic multimedia model that can be used to assess time-varying concentrations of contaminants introduced initially to subsurface soil layers or for contaminants released continuously to air, to the ground surface, or to surface water.

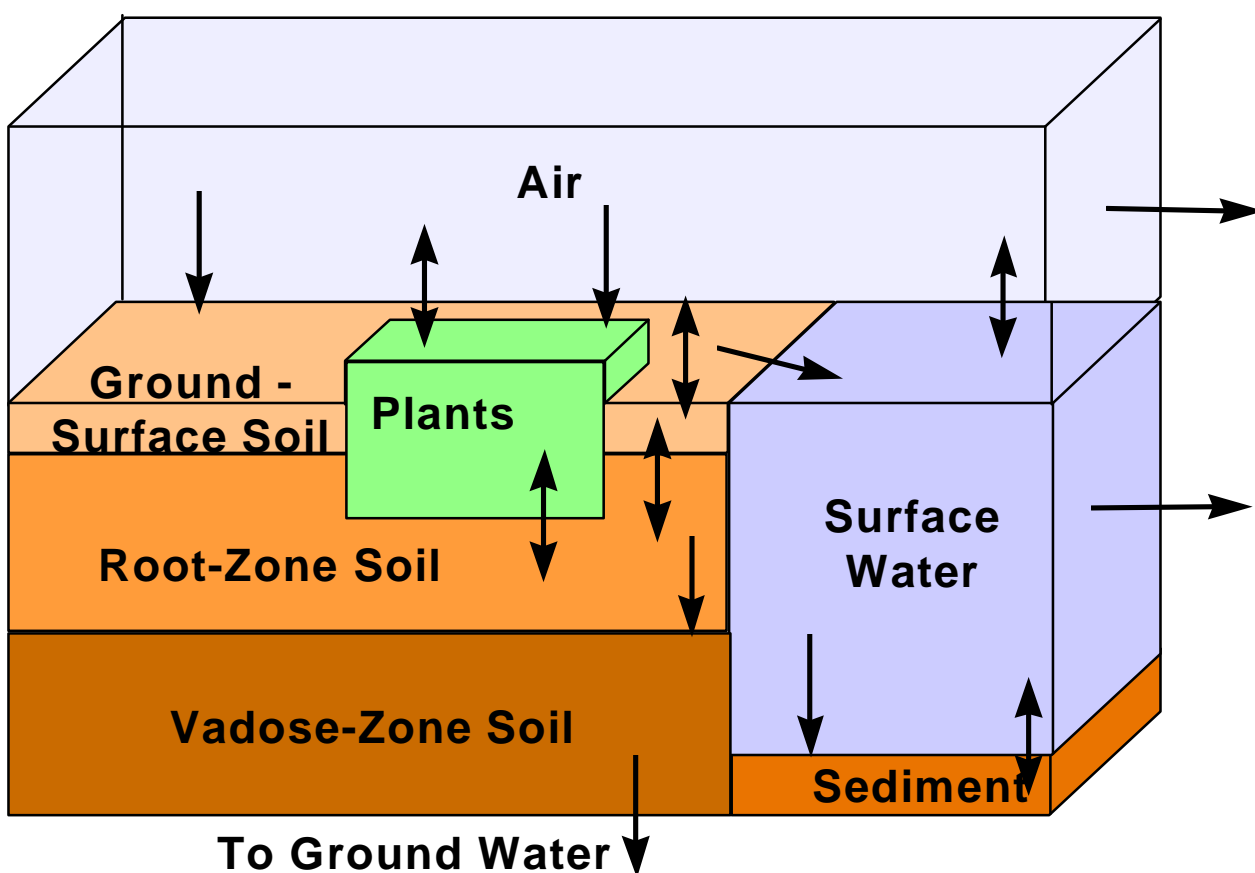
There are two major model components within CalTOX and each can operate independently of the other. The first of these two components is the multimedia transport and transformation model, which is used to determine the dispersion of soil contaminants among soil, water, and air media. The second component is the human exposure model, which translates environmental media concentrations into estimates of human contact and potential dose. A detailed description of the multimedia transport and transformation model is provided in the Part-II CalTOX report (McKone, 1993b) and detailed description of the human-exposure model is provided in the CalTOX Part-III report (McKone, 1993c). This report addresses only those modifications made to the multimedia transport and transformation model.

### **The Multimedia Transport and Transformation Model**

The 1994 version of CalTOX, that is CalTOX 1.5, is a seven-compartment regional and dynamic multimedia fugacity model. In the CalTOX framework, environmental concentrations are derived by determining the likelihood of competing processes by which chemicals (a) accumulate within the compartment of origin, (b) are physically, chemically, or biologically transformed within the compartment of origin (i.e., by hydrolysis, oxidation, etc.), or (c) are transported to other compartments by cross-media transfers that involve dispersion or advection (i.e., volatilization, precipitation, etc.). CalTOX makes use of fugacity models as a way of assessing the likelihood of mass transfer among compartments or transformation within compartments. Fugacity is a way of representing chemical activity at low concentrations. Fugacity models have been used extensively for modeling the transport and transformation of chemical contaminants in complex environmental systems (see Mackay, 1991). The fugacity approach is best suited to nonionic organic chemicals for which partitioning is related strongly to chemical properties, such as vapor pressure, solubility, and the octanol-water partition coefficient ( $K_{ow}$ ), but CalTOX has been designed to also handle ionic

organic contaminants, inorganic contaminants, radionuclides, and metals, with a modified fugacity-type approach. However, the partitioning between water and soil particles ( $K_d$ ) of ionic organic contaminants, inorganic contaminants, radionuclides, and metals are not related to  $K_{ow}$  and the fraction organic carbon in soil. Therefore, the  $K_d$  for these chemicals cannot be estimated and must be measured for each chemical at each site. For all species, fugacity and fugacity capacities are used to represent chemical potential and mass storage within compartments.

The seven-compartment structure used in CalTOX 1.5 is illustrated in Figure 1. The seven CalTOX 1.5 compartments are (1) air, (2) ground-surface soil, (3) plants, (4) root-zone soil, (5) the vadose-zone soil below the root zone, (6) surface water, and (7) sediments. The air, surface water, ground-surface-soil, plants, and sediment compartments are assumed to be in quasi-steady state with the root-zone soil, and vadose-zone soil compartments. Contaminant inventories in the root-zone soil and vadose-zone soil are treated as time-varying state variables. Contaminant concentrations in ground water are based on the leachate from the vadose-zone soil.



**Figure 1.** An illustration of mass-exchange processes modeled in the CalTOX 1.5 seven-compartment environmental transport and transformation model. (Ground water is not explicitly modeled in the system of equations but is used in the exposure calculations.)

### Balancing Gains and Losses—Sources, Transport, and Transformation

Mathematically, CalTOX addresses the inventory of a chemical in each compartment and the likelihood that, over a given period of time, that chemical will remain in the compartment, be transported to some other compartment, or be transformed into some other chemical species. Quantities or concentrations within compartments are described by a set of linear, coupled, first-order differential equations. A compartment is described by its total mass, total volume, solid-phase mass, liquid-phase mass, and gas-phase mass. Contaminants are moved among and lost from each compartment through a series of transport and transformation processes that can be represented mathematically as first-order losses. Thus, the transport and transformation equations solved in CalTOX have the form

$$\frac{d}{dt} N_i(t) = -R_i N_i(t) - \sum_{\substack{j=1 \\ j \neq i}}^m T_{ij} N_i(t) + \sum_{\substack{j=1 \\ j \neq i}}^m T_{ji} N_j(t) + S_i(t) - T_{io} N_i(t) \quad (1)$$

where,  $N_i(t)$  is the time-varying inventory of a chemical species in compartment  $i$ , mol;  $R_i$  is the first-order rate constant for removal of the species from compartment  $i$  by transformation, 1/d;  $T_{ij}$  is the rate constant for the transfer of the species from compartment  $i$  to compartment  $j$ ; and, similarly,  $T_{ji}$  is the rate constant for the transfer of the species from compartment  $j$  to compartment  $i$ , both in 1/d;  $T_{io}$  is the rate constant for the transfer of the species from compartment  $i$  to a point outside of the defined landscape system, 1/d;  $S_i$  is the source term for the species into compartment  $i$ , mole/d; and  $m$  is the total number of compartments within the landscape system.

Equation 1 is solved for the seven compartments shown in Figure 1. Since air, surface water, ground-surface soil, plants, and sediment compartments are assumed to be in quasi-steady state with the root-zone soil, and vadose-zone soil compartments, the time derivative on the left of Equation 1 is zero and gains always equal losses for these compartments. Contaminant inventories in the root-zone soil and vadose-soil zone are treated as time-varying state variables. CalTOX simulates all decay and transformation processes (such as radioactive decay, photolysis, biodegradation, etc.) as first-order, irreversible removals. Mass flows among compartments include solid-phase flows, such as dust suspension or deposition, and liquid-phase flows, such as surface run-off and ground-water recharge. The transport of individual chemical species among compartments occurs by diffusion and advection at the compartment boundaries. Each chemical species is assumed to achieve chemical equilibrium among the phases within a single compartment. For example, concentrations in the water, air and particles of the



root-zone soil layer are computed assuming chemical equilibrium among the phases. However, there is no requirement for equilibrium between adjacent compartments.

## **REVISIONS TO THE MULTIMEDIA MASS-BALANCE EQUATIONS**

In CalTOX 1.5, contaminant sources can be introduced to five of the CalTOX compartments—air, ground-surface soil, root-zone soil, vadose-zone soil, and surface water. However, in root-zone soil and vadose-zone soil, the source can only be specified as either zero or as an initial concentration (batch input). For the uncontrolled hazardous waste sites to which CalTOX 1.5 is currently applied, this type of source is used to represent the original and typically unknown placement of toxic chemicals in soils. In these cases, the CalTOX model is used to assess how the slow decay and migration of these soil-layer deposits determine both concentrations in the soil layers and the concentrations in adjacent environmental media. The sources to air, ground-surface soil, and surface water, can be specified either as zero or as a continuous input, i.e. mass per unit time. This latter type of source is used to represent such things as atmospheric emissions, pesticide applications, surface-water discharges, and other types of regional and continuous non-point pollution.

In this section two modifications are discussed. First, we describe the modification that allows the specification of either a batch or continuous input to the root-zone soil compartment. Second, we discuss the approach used to calculate time-averaged environmental media concentrations, which serve as the output from the multimedia transport and transformation analysis. Rather than reporting concentrations and fugacities at a specified time, as was done in CalTOX 1.5, these state variables are now averaged over the exposure duration, ED.

### **Including Both Batch and Continuous Inputs to the Root-Zone Soil**

In order to make the CalTOX model more applicable to a broader range of environmental problems, it has been modified so that batch inputs, continuous inputs or zero inputs can be specified for the root- zone soil.

### **Average Compartment Inventories Over the Exposure Duration**

The CalTOX model has been modified so that rather than specifying the time-dependent compartment fugacities, concentrations, and inventories at a specific time, these state variables are now reported as the average value over the exposure duration, ED. This allows for better use of the model for comparisons. Nevertheless, CalTOX still provides a table listing the time history of the root-soil, vadose-zone, and ground-water compartment inventories as well as the time history of annual daily intake.

### The Revision of CalTOX Gain-Loss Equations

With addition of the source term to root-zone soil, the dynamic and steady-state gains and losses in each of the seven compartments currently used in CalTOX are expressed by the equations below. These equations differ little from the equations used in the 1993 CalTOX report (McKone, 1993b).

$$L_a N_a = S_a + T_{pa} N_p + T_{ga} N_g + T_{wa} N_w \quad (\text{air}) \quad (2)$$

$$L_p N_p = T_{ap} N_a + T_{sp} N_s \quad (\text{plants}) \quad (3)$$

$$L_g N_g = S_g + T_{ag} N_a + T_{sg} N_s \quad (\text{ground-surface soil}) \quad (4)$$

$$\frac{dN_s}{dt} = -L_s N_s + S_s + T_{gs} N_g \quad (\text{root soil}) \quad (5)$$

$$\frac{dN_v}{dt} = -L_v N_v + T_{sv} N_s \quad (\text{vadose soil}) \quad (6)$$

$$L_w N_w = S_w + T_{aw} N_a + T_{gw} N_g + T_{dw} N_d \quad (\text{surface water}) \quad (7)$$

$$L_d N_d = T_{wd} N_w \quad (\text{sediments}) \quad (8)$$

In these equations, the  $N$ 's represent time-varying compartment inventories and the  $T_{ij}$  ( $i, j = a, p, g, s, v, w, \text{ or } d$ ) are transfer rate constants, with units of  $\text{day}^{-1}$ , that express the fraction per unit time of the inventory of compartment  $i$  that is transferred to compartment  $j$ . The compartment abbreviations are  $a$  for air,  $p$  for plants,  $g$  for ground-surface soil,  $s$  for root-zone soil,  $v$  for vadose-zone soil,  $w$  for surface water, and  $d$  for sediments. The product of an  $N$  term and a  $T$  term is the rate of change of inventory in mol/d.  $L_i N_i$  represents all losses from compartment  $i$ , mol/d. The terms  $S_a$ ,  $S_g$ ,  $S_s$ , and  $S_w$ , in Equations 2, 4, 5, and 7 are the rates of contaminant input to the air, ground-surface-soil, root-zone soil, and surface water compartments, mol/d. The rate constants  $T_{ij}$  are described in the CalTOX report (McKone, 1993b) in terms of landscape properties, chemical properties, and fugacity capacities. Loss rate constants are defined in terms of transfer and transformation rate constants. With the exception of the plants

and soils compartment described in the next section, these definitions remain unchanged.

As revised for the added source term to root soil and the time-averaging of the compartment inventories, the solution to Equations 2 to 8 are now take the form

$$N_v(t) = \mathbf{a}_7 \exp(-L_v t) + \mathbf{a}_8 \exp(-I_1 t) + \mathbf{b}_5 , \quad (9)$$

$$N_s(t) = \mathbf{a}_6 \exp(-I_1 t) + \mathbf{b}_4 , \quad (10)$$

$$\bar{N}_v(\text{ED}) = \frac{\int_{t_0}^{t_0+\text{ED}} N_v(t) dt}{\text{ED}} \quad (11)$$

$$\bar{N}_s(\text{ED}) = \frac{\int_{t_0}^{t_0+\text{ED}} N_s(t) dt}{\text{ED}} \quad (12)$$

where  $t_0$  is the time, in years, after initial contaminant placement in soil when exposure begins and ED is the exposure duration, in years;

$$N_g(\text{ED}) = \mathbf{a}_5 \bar{N}_s(\text{ED}) + \mathbf{b}_3 , \quad (13)$$

$$N_a(\text{ED}) = \mathbf{a}_3 N_g(\text{ED}) + \mathbf{a}_4 \bar{N}_s(\text{ED}) + \mathbf{b}_2 , \quad (14)$$

$$N_w(\text{ED}) = \mathbf{a}_1 N_a(\text{ED}) + \mathbf{a}_2 N_g(\text{ED}) + \mathbf{b}_1 , \quad (15)$$

$$N_d(\text{ED}) = \frac{T_{\text{wd}}}{L_d} N_w(\text{ED}) , \text{ and} \quad (16)$$

$$N_p(\text{ED}) = \frac{T_{ap}}{L_p} N_a(\text{ED}) + \frac{T_{gp}}{L_p} N_g(\text{ED}) + \frac{T_{sp}}{L_p} \bar{N}_s(\text{ED}) \quad (17)$$

In these expressions, the term (ED) adjacent to each inventory,  $N_i$ , indicates that the estimated inventory applies to the exposure duration, ED. In the case of the root-soil and vadose-zone compartments, these inventories reflect time-averaged inventories. In the case of the other compartments, these inventories reflect the steady-state relationship of a compartment with the two soil compartments. The parameters used in these expressions have the following definitions.

$$\lambda_1 = L_s - T_{gs} \mathbf{a}_5 \quad , \quad (18)$$

$$\mathbf{a}_8 = \frac{T_{sv} \mathbf{a}_6}{(L_v - \lambda_1)} \quad , \quad (19)$$

$$\mathbf{a}_7 = N_v(0) - \frac{T_{sv} \mathbf{a}_6}{(L_v - \lambda_1)} - \frac{T_{sv} \mathbf{b}_4}{L_v} \quad , \quad (20)$$

$$\mathbf{a}_6 = N_s(0) - \frac{T_{gs} \mathbf{b}_3 + S_s}{\lambda_1} \quad (21)$$

$$\mathbf{a}_5 = \frac{\left[ T_{ag} \mathbf{a}_4 + \frac{T_{pg} T_{ap}}{L_p} \mathbf{a}_4 + \frac{T_{pg} T_{sp}}{L_p} + T_{sg} \right]}{\left[ L_g - T_{ag} \mathbf{a}_3 - \frac{T_{pg} T_{ap}}{L_p} \mathbf{a}_3 - \frac{T_{pg} T_{gp}}{L_p} \right]} \quad , \quad (22)$$

$$\mathbf{a}_4 = \frac{\left[ \frac{T_{pa} T_{sp}}{L_p} \right]}{\left[ L_a - \frac{T_{pa} T_{ap}}{L_p} - T_{wa} \mathbf{a}_1 \right]} \quad , \quad (23)$$

$$\mathbf{a}_3 = \frac{\left[ \frac{T_{pa} T_{gp}}{L_p} + T_{wa} \mathbf{a}_2 + T_{ga} \right]}{\left[ L_a - \frac{T_{pa} T_{ap}}{L_p} - T_{wa} \mathbf{a}_1 \right]}, \quad (24)$$

$$\mathbf{a}_2 = \frac{T_{gw}}{\left[ L_w - \frac{T_{wd} T_{dw}}{L_d} \right]}, \quad (25)$$

$$\mathbf{a}_1 = \frac{T_{aw}}{\left[ L_w - \frac{T_{wd} T_{dw}}{L_d} \right]}, \quad (26)$$

$$\mathbf{b}_5 = \frac{T_{sv} \mathbf{b}_4}{L_v}, \quad (27)$$

$$\mathbf{b}_4 = \frac{T_{gs} \mathbf{b}_3 + S_s}{\lambda_1} \quad (28)$$

$$\mathbf{b}_3 = \frac{\left[ S_g + T_{ag} \mathbf{b}_2 + \frac{T_{pg} T_{ap}}{L_p} \mathbf{b}_2 \right]}{\left[ L_g - T_{ag} \mathbf{a}_3 - \frac{T_{pg} T_{ap}}{L_p} \mathbf{a}_3 - \frac{T_{pg} T_{gp}}{L_p} \right]}, \quad (29)$$

$$\mathbf{b}_2 = \frac{\left[ S_a + T_{wa} \mathbf{b}_1 \right]}{\left[ L_a - \frac{T_{pa} T_{ap}}{L_p} \mathbf{a}_3 - T_{wa} \mathbf{a}_1 \right]}, \text{ and} \quad (30)$$

$$\mathbf{b}_1 = \frac{S_w}{\left[ L_w - \frac{T_{wd} T_{dw}}{L_d} \right]}. \quad (31)$$

## **MODIFICATIONS TO SOIL/PLANT MODELING IN CALTOX**

In the CalTOX 1.5 model, vegetation is modeled as a single compartment consisting of air, water, plant lipids and other materials. Both the plant roots and above ground plant mass are included in this compartment. The fugacity capacity of this compartment was based on a simplified version of the model proposed by Paterson and Mackay (1989). In addition, it was assumed that, for nonionic organic chemicals, the fugacity in the total plant mass (that is, both roots and above-ground biomass) is the average of that in the root-zone soil and the air. This implied that the fugacity in the plants is the average of the root-zone soil and air fugacities. For ionic organic chemicals and inorganic species, the fugacity in the plant tissues was assumed equal to that of the soil when equilibrium is attained. This approach resulted in some calculational problems and was not consistent with more recent concepts of plant uptake as published by Paterson et al. (1994).

### **The Revised Air/Soil/Plant Model**

In order to improve the reliability of the plant/air/soil interaction model in CalTOX and to bring it into consistency with the recent work of Paterson et al. (1994), several modifications were made. These modifications are described below. The principal modification of the plants compartment was to include only above-ground vegetation in what is called the “plants” compartment. This was done because the above ground portion of plants strive to reach fugacity equilibrium with the air compartment and are little impacted by the soil. The portion of vegetation below the ground surface has now been added as a separate phase to the root-soil compartment. This change was made to reflect the large exchange surface that root tissues have with soil and soil solution.

In the revised plant model, the above ground vegetation is modeled as interacting with the soil solution and with the air compartment. The interaction of above-ground plant tissues (primarily leaves) with the root-soil compartment is by root uptake and translocation through the transpiration stream going up the xylem tubes and the transport of nutrients (sugars) down the phloem tubes. The interaction of plants with the air compartment is by diffusion of gas-phase contaminants through the stomata, diffusion of gas-phase contaminants through the cuticle tissue as a result of partitioning from air, and the accumulation and diffusion of solid-phase contaminant that has been deposited on leaf surfaces. The revised modeling scheme is illustrated in Figure 2.

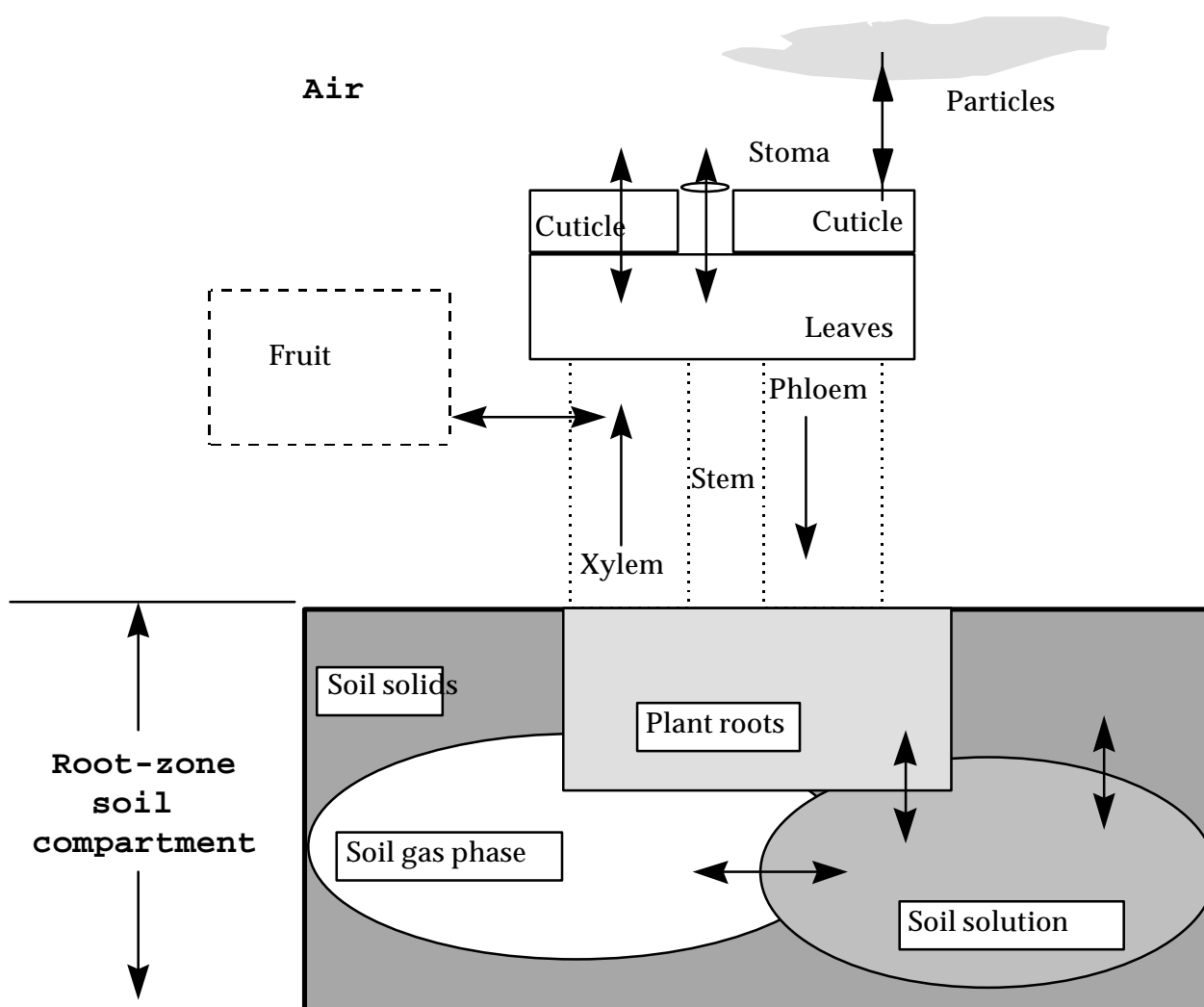


Figure 2. The structure of the revised plants compartments in CalTOX. Contaminants enter plants from either air or root soil. Transfer between air and plant is by deposition onto leaf surfaces with diffusion through the cuticle or by air exchange through the stomata. Transfer between leaves and roots is through phloem and xylem. Transfer from soil to roots is by water transfer from soil to roots. Exchange between air and soil is by deposition, dust resuspension, and diffusion at the soil/air boundary.

### Changes to Fugacity Capacities

In order to incorporate the revised plants model into CalTOX, the following fugacity capacity terms have been modified or added in the CalTOX spreadsheet.

*Fugacity capacity of the root-soil compartment,  $Z_s$*

With the inclusion of the plant roots as a thermodynamic phase within the root-zone-soil compartment, the fugacity capacity of the root-zone-soil compartment is now given by

$$Z_s = a_s \times Z_{\text{air}} + b_s \times Z_{\text{water}} + vol_{\text{pr}} \times Z_{\text{pr}} + (1 - a_s - b_s - vol_{\text{pr}}) \times Z_{\text{sp}} \quad (32)$$

where  $\alpha_s$  is the volume fraction of air in the soil compartment;  $Z_{\text{air}}$  is the fugacity capacity of the soil gas phase, mol/m<sup>3</sup>-Pa;  $\beta_s$  is the volume fraction of water in the compartment;  $Z_{\text{water}}$  is the fugacity capacity of the soil liquid phase, mol/m<sup>3</sup>-Pa;  $vol_{\text{pr}}$  is the volume fraction of the root-zone soil occupied by plant roots;  $Z_{\text{pr}}$  is the fugacity capacity of plant roots, mol/m<sup>3</sup>-Pa;  $(1 - \alpha_s - \beta_s - vol_{\text{pr}})$  is the volume fraction of soil solids in the compartment; and  $Z_{\text{sp}}$  is the fugacity capacity of the soil particles, mol/m<sup>3</sup>-Pa.  $Z_{\text{air}}$  is equal to  $1/RT$  where  $R$  is the universal gas constant, 8.314 Pa-m<sup>3</sup>/mol-°K, and  $T$  is temperature in kelvins (°K). The fugacity capacity in *pure water*,  $Z_{\text{water}}$ , is given by  $1/H$  where  $H$  is the Henry's law constant, Pa-m<sup>3</sup>/mol.

The volume fraction of the soil compartment that is plant-roots,  $vol_{\text{pr}}$ , is estimated as

$$vol_{\text{pr}} = 0.5 \times \frac{bio_{\text{inv}} \text{ Area}}{bio_{\text{dm}} r_p V_s} \quad (33)$$

where 0.5 is the assumed fraction of plant inventory that is below ground;  $bio_{\text{inv}}$  is the dry-mass inventory of the vegetation, kg(dry-mass vegetation)/m<sup>2</sup>;  $bio_{\text{dm}}$  is the ratio of vegetation dry to fresh mass;  $r_p$  is the density of the fresh plant roots, kg/m<sup>3</sup>; and  $V_s$  is the volume of the root-soil compartment, m<sup>3</sup>.

*Fugacity capacity of plant roots,  $Z_{\text{pr}}$*

The fugacity capacity of the plant roots is determined indirectly from the plant-soil partition coefficient and the fugacity capacity of the non-root portion of the soil compartment,

$$Z_{\text{pr}} = \frac{K_{\text{ps}} \times [a_s \times Z_{\text{air}} + (b_s \times Z_{\text{water}}) + Z_{\text{sp}} \times (1 - a_s - b_s)] \times r_p}{r_s (1 - a_s - b_s)} \quad (34)$$



where  $K_{ps}$  is the fresh-mass plant-root/soil partition coefficient, mol/kg(plant) per mol/kg(soil) and  $\rho_s$  is the density of the soil compartment, kg/m<sup>3</sup>.

*Fugacity capacity of above-ground plant biomass*

The fugacity capacity,  $Z_p$  in mol/m<sup>3</sup>-Pa, assigned to the above-ground plant biomass takes two forms depending on whether the contaminant of interest is a non-ionic organic chemical with a non-zero vapor pressure or a speciating chemical, such as metal compound or dissociating organic compound. For a non-ionic organic chemical with a non-zero vapor pressure,  $Z_p$  is given by

$$Z_p = (K_{pa} \times r_p \times Z_{air}) + (K_{pa}^{part} \times \rho_p \times Z_{ap} \times rb_a / rs_g) \quad \text{when } Z_{air} > 0 \quad (35)$$

and for a speciating chemical with no vapor pressure,

$$Z_p = K_{pa}^{part} \times r_p \times Z_{ap} \times rb_a / rs_g \quad \text{when } Z_{air} = 0 \quad (36)$$

In these expressions,  $K_{pa}$  is the plant/air-vapor partition ratio, that expresses the equilibrium ratio of contaminant concentration in plant leaves (mol/kg-plant) to contaminant concentration in the gas phase of the air, (mol/m<sup>3</sup>-air). In the absence of measured values,  $K_{pa}$  can be estimated as

$$K_{pa} = [0.5 + (0.4 + 0.01 K_{ow}) \times R \times T \times Z_{water}] / r_p \quad \text{for gases.} \quad (37)$$

$K_{pa}^{part}$  is the plant/air-particle partition ratio.  $K_{pa}^{part}$  expresses the equilibrium ratio of contaminant concentration in plant leaves (mol/kg-plant) to contaminant concentration in the particle phase of the air, (mol/m<sup>3</sup>-air). This ratio is independent of chemical species. McKone and Ryan (1989) have shown that, based on a mass balance of deposition and wash-off, this ratio is on the order of 3000 mol/kg(plant) per mol/m<sup>3</sup>(air).  $Z_{ap}$  is the fugacity capacity of atmospheric particles, mol/m<sup>3</sup>-Pa.  $rb_a$  is the dust load of the atmosphere, kg/m<sup>3</sup>, and  $rs_g$  is the density, kg/m<sup>3</sup>, of the solid phase of the surface soil that is assumed to provide the atmospheric dust load.

*Fugacity capacity of phloem liquid,  $Z_{phl}$*

The phloem solution is comprised of nutrients, primarily sugars, dissolved in water. One issue that is not easily addressed is the extent to which the phloem liquid contains a lipid component. We divide the phloem liquid into two phases, a water phase and the non-water phase. The fugacity capacity of the non-water phase is

designated  $Z_{\text{phl\_other}}$  and is used to account for the nutrients, sugars, and any lipids that may be suspended in this phase. In the absence of measured data, the fugacity capacity of the “other” phloem phase,  $Z_{\text{phl\_other}}$ , is assumed negligible and equal to zero. The total fugacity capacity of the phloem liquid,  $Z_{\text{phl}}$  in mol/m<sup>3</sup>-Pa, is the volume-weighted combination of the two phases, water and other,

$$Z_{\text{phl}} = (1 - f_{\text{other}}) \times Z_{\text{water}} + f_{\text{other}} \times Z_{\text{phl\_other}} \quad (38)$$

$f_{\text{other}}$  is the volume fraction of the phloem solution that is nutrients, sugars, and suspended materials and is assigned a default value of 0.01. The remaining volume fraction of 0.99 is assumed to be water.

### Changes to Plant Mass Transfer Rate Constants

In order to incorporate the revised plant model into CalTOX, the following transfer-rate constants have been modified or added in the CalTOX spreadsheet.

*Between air and plants,  $T_{\text{ap}}$ ,  $T_{\text{pa}}$*

The mass transfer rate constants,  $T_{\text{ap}}$  and  $T_{\text{pa}}$ , express the likelihood per unit time that a contaminant molecule will transfer, respectively from air to plant or from plant to air. In the revised model, these terms are estimated as

$$T_{\text{ap}} = \frac{Z_{\text{air}} \times \frac{\text{LAI}}{r_{\text{stom}}} + Y_{\text{ap}} \times \text{LAI} + \frac{\rho b_a}{\rho s_s} \times V_{\text{int}} \times V_{\text{dep}} \times Z_{\text{ap}}}{Z_a \times d_a} \quad (39)$$

$$T_{\text{pa}} = \frac{Z_{\text{air}} \times \frac{\text{LAI}}{r_{\text{stom}}} + Y_{\text{ap}} \times \text{LAI} + \frac{\rho b_a}{\rho s_s} \times V_{\text{int}} \times V_{\text{dep}} \times Z_{\text{ap}}}{Z_p \times d_p} \quad (40)$$

Implicit in Equation 40 is the assumption that the rate of particle deposition on to leaf surfaces is balanced by the removal of these particles by wind and wash off. In these expressions, LAI is the leaf area index, the ratio of vegetation surface area to land area and  $r_{\text{stom}}$  is the resistance to contaminant mass transfer through the plant stomata, d/m, and is estimated by scaling to the mass transfer resistance for water vapor

$$r_{\text{stom}} = D_{\text{wv-air}} \times r_{\text{wv-stom}} / D_{\text{air}} \quad (41)$$

where  $D_{\text{wv-air}}$  is the diffusion coefficient of water vapor in air,  $\text{m}^2/\text{d}$ ,  $r_{\text{wv-stom}}$  is the stomata resistance to water vapor,  $\text{d}/\text{m}$ , and  $D_{\text{air}}$  is the diffusion coefficient of the contaminant in air,  $\text{m}^2/\text{d}$ .  $D_{\text{wv-air}}$  is on the order of  $2.1 \text{ m}^2/\text{d}$  and  $r_{\text{wv-stom}}$  is on the order of  $0.0027 \text{ m}/\text{d}$ .  $Y_{\text{ap}}$  is the fugacity-mass transfer coefficient between air and through the soil layer on the plant surfaces and is given as

$$Y_{\text{ap}} = \left[ \frac{\delta_{\text{ap}}}{Z_{\text{air}} \times D_{\text{air}}} + \frac{\delta_{\text{slyr}}}{Z_{\text{s}} \times D_{\text{s}}} \right]^{-1} \quad (42)$$

where  $d_{\text{ap}}$  is the effective boundary layer thickness between air and plant leaves and is assumed to be on the order of  $0.005 \text{ m}$ ;  $\delta_{\text{slyr}}$  is the thickness of the soil layer on the plant surface and is estimated to be on the order of  $5 \times 10^{-6} \text{ m}$ ; and  $Z_{\text{s}}$  is the fugacity capacity of the soil material on plants,  $\text{mol}/\text{m}^3\text{-Pa}$ . Of the remaining parameters in Equation 39,  $V_{\text{int}}$  is the fraction of material deposited from air to ground that is intercepted by vegetation, which based on the model of Whicker and Kirchner (1987) is estimated as

$$V_{\text{int}} = 1 - \exp(-2.8 \text{ bio}_{\text{inv}}) \quad (43)$$

Finally,  $V_{\text{dep}}$  is the effective deposition velocity for particles from air onto plant and ground surfaces and is on the order of  $300 \text{ m}/\text{d}$ ;  $d_{\text{a}}$  is the mixing height of the atmosphere compartment,  $\text{m}$ ; and  $d_{\text{p}}$  is the effective depth of the plants compartment and is equal to the mass,  $\text{bio}_{\text{inv}}$  divided by the density of the plants compartment,  $r_{\text{p}}$ .

*Between ground-surface soil and plants,  $T_{\text{gp}}$ ,  $T_{\text{pg}}$*

The mass transfer rate constants,  $T_{\text{gp}}$  and  $T_{\text{pg}}$ , express the likelihood per unit time that a contaminant molecule will transfer, respectively from ground-surface soil to plants or from plant to ground-surface soil. In the revised model, these terms are estimated as

$$T_{\text{gp}} = 0 \quad (44)$$

$$T_{\text{pg}} = 1/180 \text{ d}^{-1} \quad (45)$$

Equation 44 reflects the assumption that there are no significant pathways by which contaminants move from the ground-soil surface to leaves. Equation 45 reflects the assumption that mass of contaminant in the plant leaves and stems are carried to the ground surface through leaf loss and senescence with an effective lifetime of 180 days.

Between root-zone soil and plants,  $T_{sp}$ ,  $T_{ps}$

The mass transfer rate constants,  $T_{sp}$  and  $T_{ps}$ , express the likelihood per unit time that a contaminant molecule will transfer, respectively from root-zone soil to plants or from plants to root-zone soil. In the revised model, these terms are estimated as

$$T_{sp} = \frac{\text{transpire} \times Z_{\text{water}}}{Z_s d_s} \quad (46)$$

$$T_{ps} = \frac{\text{Phlm}_{\text{flow}} \times Z_{\text{phl}}}{Z_p d_p} \quad (47)$$

where *transpire* is the flux of water that moves from soil into the roots and up through the plant as a result of transpiration, m/d; *Phlm<sub>flow</sub>* is the flux of fluid that moves from plant tissues down into the roots through the phloem tubes, m/d; and *Z<sub>phl</sub>* is the fugacity capacity of the phloem solution. Both of these fluxes represent fluid flows with actual units of m<sup>3</sup> of fluid per m<sup>2</sup> of soil. The area correction is included in the parameter values calculated on an area basis. Because phloem flows are usually much less than transpiration flows, *Phlm<sub>flow</sub>* is estimated as 1/10 times the transpiration rate in m/d.

**SOIL CONCENTRATIONS THAT EXCEED THE FUGACITY-CAPACITY LIMIT AS NON-AQUEOUS-PHASE MASS (NAPM)**

Within a multimedia transport and transformation model such as CalTOX, each environmental compartment forms a unit in which one can balance gains and losses attributable to sources, transfers to and from other compartments, and physicochemical transformations. Earlier versions of the CalTOX model were designed for assessing the behavior of contaminants at low concentration. "Low concentration" implies that the chemical concentration in any phase within a compartment is well below the solubility limit of that phase. In a fugacity model such as CalTOX, this solubility limit translates into a fugacity limit, which is defined by the solubility limit in the soil solution. For example, the soil of a hazardous waste site could contain benzene at or close to its saturation or maximum fugacity. The saturation fugacity is the partial pressure of benzene in the gas phase of soil when the gas phase is in equilibrium with the water phase and benzene is at its solubility limit in the water phase. This pressure cannot be exceeded even when there is pure-phase chemical present in soil. This pressure represents the maximum escaping tendency of benzene and thus its driving force for migration out of the site. A gradient in fugacity thus exists from the waste to the adjacent environmental media of air, water, soil, vegetation and animals. However, so long as the pure-phase chemical remains, the fugacity exerted by benzene within the soil phase will be maintained at the fugacity limit. Once the pure-phase benzene has been depleted, the fugacity of benzene in the soil will begin to diminish. The length of time this takes will depend on the total inventory of chemical in the soil layer, the fugacity gradient between soil and air and the resistance offered by any engineered barriers.

In order to address this problem, the CalTOX model was modified so that mass transfer at concentrations that exceed the soil fugacity limit can be simulated using CalTOX. The modification was applied to the root-zone soil compartment, but also impacts the vadose-zone soil compartment. The modification to CalTOX allows any contaminant in the root zone to exist in a distributed non-aqueous-phase mass (NAPM). The contaminant NAPM behaves as a separate phase that exists as a reservoir of specified mass that can maintain the soil compartment at saturation fugacity until the original volume of pure chemical is depleted. After the pure phase is depleted, the transport and transformation of a chemical in soil layers is simulated according to the first order kinetics that are used in the earlier versions of the CalTOX model under the assumption of no NAPM phase. It should be noted that these modifications to CalTOX allow the treatment of distributed, non-moving NAPM. The equations do not treat non-aqueous phase liquid (NAPL) flow.

The process of adding a NAPM phase to CalTOX begins with the specification of the saturation inventory corresponding to the fugacity limit in that compartment. In the root-zone soil compartment, the saturation inventory in mol is defined as  $N_s^{sat}$  and is estimated from soil properties as

$$N_s^{sat} = \frac{S}{Z_{water}} \times Z_s \times V_s = VP \times Z_s \times V_s \quad (48)$$

where  $S$  is the water solubility limit of the contaminant, mol/m<sup>3</sup>;  $Z_{water}$  is the fugacity capacity of pure water, mol/m<sup>3</sup>-Pa;  $Z_s$  is the fugacity capacity of the root-zone soil compartment, mol/m<sup>3</sup>-Pa;  $V_s$  is the total volume of the root-zone compartment, m<sup>3</sup>; and  $VP$  is the vapor pressure exerted above the pure phase of the contaminant at standard temperature and pressure, in Pa. As is shown in this equation, the saturation inventory is the same whether it is based on  $VP$  or  $S$ .

### Root-Zone Soil Compartment

The mass balance equation for the root-zone soil inventory was identified in Equation 5 as

$$\frac{dN_s}{dt} = -L_s N_s + S_s + T_{gs} N_g \quad (\text{root soil}) \quad (49)$$

This equation was based on the assumption that the rate of loss of inventory is proportional to the total inventory in the soil. When the soil inventory exceeds the saturation value, this is not the case. It should be noted that contaminant inventory in excess of the saturation inventory, can exist in the soil, but it can not exist in the gas, liquid, or solid (organic) phases that were used to determine the fugacity capacity of the soil. In addition, when there is contaminant in soil in excess of the fugacity capacity, it is assumed that all transport and transformation processes apply only to the saturation inventory and not to the total inventory. The basis for this assumption is that loss mechanisms and diffusion and advection processes take place within the vapor or liquid phase and the amount of contaminant in these phases is limited by the saturation fugacity. Thus, we must consider that, potentially, the soil layer has two inventories—the actual inventory,  $N_{s\text{-actual}}$ , which includes both the saturation inventory and the NAPM phase contaminant, and the observed inventory  $N_{s\text{-observed}}$ , which is the inventory used to make mass transfer calculations and reflects the chemical potential exerted by the soil compartment.  $N_{s\text{-observed}}$  must be less than or equal to  $N_s^{sat}$ . As long as the actual soil-compartment inventory is equal to or above the saturation

inventory, then the observed inventory is not changing and the actual inventory is changing at a rate that is independent of the actual inventory and only dependent on the saturation inventory, which is a constant. Under these conditions Equation 49 takes on two forms to reflect the “observed” and “actual” inventory of the soil,

$$\frac{dN_{s\text{-observed}}(t)}{dt} = 0 \quad [\text{when } N_{s\text{-actual}}(t) \geq N_s^{\text{sat}}] \quad (50)$$

$$\frac{dN_{s\text{-actual}}(t)}{dt} = -L_s N_s^{\text{sat}} + S_s + T_{gs} N_g \quad [\text{when } N_{s\text{-actual}}(t) \geq N_s^{\text{sat}}] \quad (51)$$

and since

$$N_g(t) = \mathbf{a}_5 N_s(t) + \mathbf{b}_3 \quad (52)$$

then

$$\begin{aligned} \frac{dN_{s\text{-actual}}(t)}{dt} &= -L_s N_s^{\text{sat}} + S_s + T_{gs}(\mathbf{a}_5 N_s^{\text{sat}} + \mathbf{b}_3) \\ &= \text{const}_{\text{sat}} \quad [\text{when } N_{s\text{-actual}}(t) \geq N_s^{\text{sat}}] \quad (53) \end{aligned}$$

Consider now what happens mathematically in the soil compartment during an arbitrary time interval from  $t_i$  to  $t_{i+1}$ . If during this entire interval  $N_{s\text{-actual}}$  is greater than or equal to  $N_s^{\text{sat}}$ , then

$$N_{s\text{-actual}}(t_{i+1}) = N_{s\text{-observed}}(t_i) = N_s^{\text{sat}} \quad (54)$$

and

$$N_{s\text{-actual}}(t_{i+1}) = N_{s\text{-actual}}(t_i) + \text{const}_{\text{sat}} \times (t_{i+1} - t_i) \quad (55)$$

where

$$const_{sat} = -L_S N_S^{sat} + S_S + T_{gs}(\mathbf{a}_5 N_S^{sat} + \mathbf{b}_3) \quad (56)$$

In contrast, if during the entire interval  $t_i$  to  $t_{i+1}$ ,  $N_{S-actual}$  is always less than  $N_S^{sat}$ , then the “observed” and “actual” solutions to Equation 49 are

$$N_{S-observed}(t_{i+1}) = N_{S-actual}(t_{i+1}) \quad (57)$$

$$N_{S-actual}(t_{i+1}) = N_{S-actual}(t_i) \times \exp[-\lambda_1 \times (t_{i+1} - t_i)] + \mathbf{b}_4 \quad (58)$$

where, as stated earlier,  $\lambda_1$  is equal to  $L_S - T_{gs} \mathbf{a}_5$  and  $\mathbf{b}_4$  is equal to  $(T_{gs} \mathbf{b}_3 + S_S)/\lambda_1$ .

These solutions are incorporated into CalTOX by selecting time intervals for the estimation of compartment inventories so that, if the saturation inventory is exceeded, the time steps break at exactly the point when the inventory shifts from a saturated inventory to a non-saturated inventory. The added equations do not treat nonaqueous phase liquid (NAPL) flow.

### Vadose-Zone Soil Compartment

Even though the contaminant concentration in the vadose zone is still not allowed to exceed the saturation limit, allowing the root-zone soil to exceed saturation means that contaminant concentrations in the vadose zone must be estimated based on conditions in the root soil. As was noted above, the differential mass balance equation describing the contaminant inventory in the vadose zone is

$$\frac{dN_V}{dt} = -L_V N_V + T_{SV} N_S \quad (\text{vadose soil}) \quad (59)$$

Once again, we consider what happens mathematically in the soil compartments during an arbitrary time interval from  $t_i$  to  $t_{i+1}$ . If during this entire interval  $N_{S-actual}$  is greater than or equal to  $N_S^{sat}$ , then Equation 59 becomes

$$\frac{dN_V}{dt} = -L_V N_V + T_{SV} N_S^{sat} \quad (60)$$

and the solution for this expression is



$$N_v(t_{i+1}) = N_v(t_i) \exp[-L_v (t_{i+1}-t_i)] + \{1-\exp[-L_v (t_{i+1}-t_i)]\} \times \frac{T_{sv}N_s^{sat}}{L_v} \quad (61)$$

Otherwise, if during the entire interval from  $t_i$  to  $t_{i+1}$ ,  $N_{s-actual}$  is less than  $N_s^{sat}$ , then the solution to Equation 59 follows the form given earlier in Equation 9. The shift between the two alternate solutions is facilitated by selecting the time steps so that there is a break at exactly the point when the inventory shifts from a saturated inventory to a non-saturated inventory. Figure 3 illustrates how the modeled and true solutions for the inventories in root soil and the actual inventory in vadose soil appear when the root-soil concentration starts out above the saturation limit.

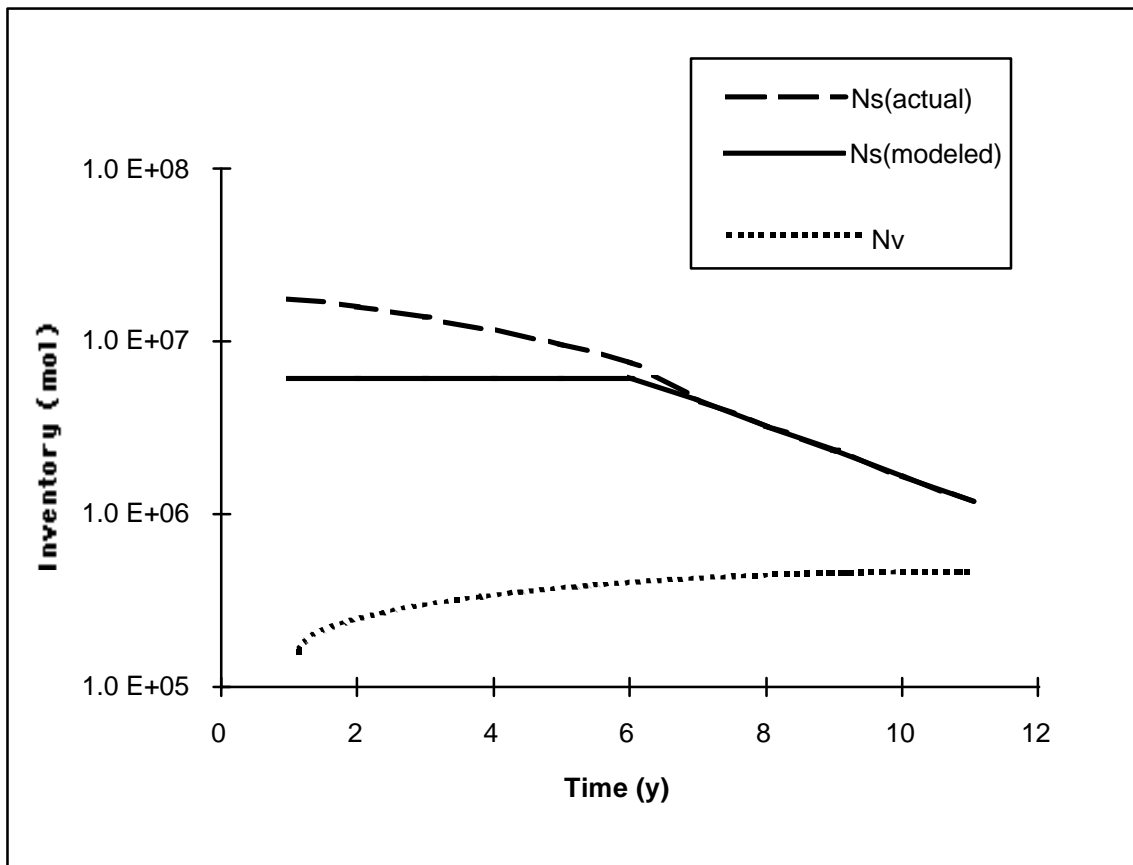
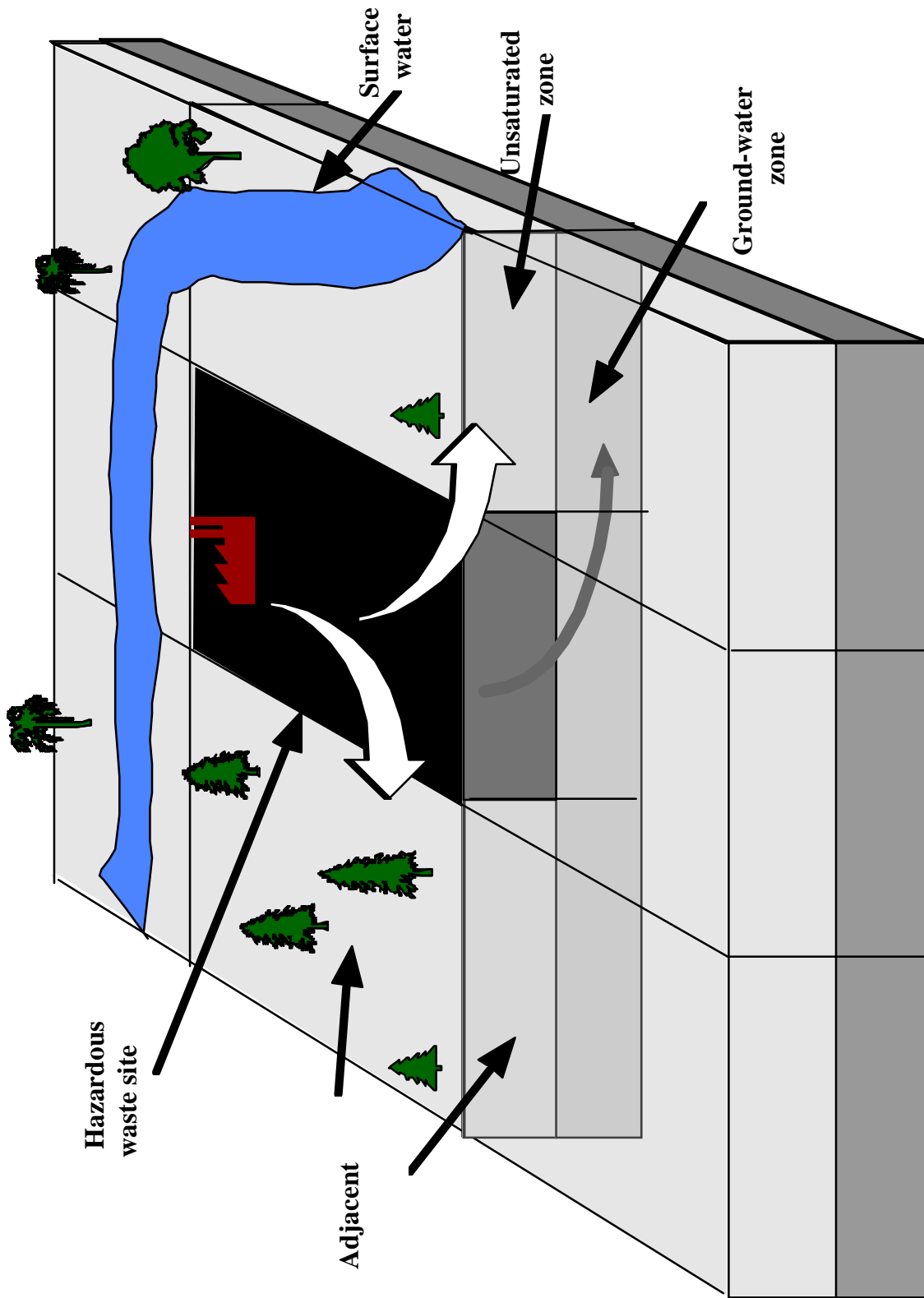


Figure 3. The modeled and true solution for contaminant inventories in root soil and the actual inventory in vadose soil when the root-soil concentration starts out above the saturation limit

**OFF-SITE TRANSFERS IN AIR AND GROUND WATER**

In version 1.5, CalTOX addressed human exposures as those coincident with the contaminated landscape. Off-site transfers were not addressed. The CalTOX 2.3 spreadsheet has now been modified so that concentrations of contaminants in environmental media adjacent to the contaminated site can be estimated. The modifications address the transfer of contaminants off site by air and ground water. The relationship between the contaminated site and adjacent landscapes is illustrated in Figure 4. In the sections below, modifications for transfers in air and ground water are discussed respectively.



### Contamination of Adjacent Landscape Media by Air Transport Off Site

Gases and particles can be transferred away from the hazardous-waste landfill or contaminated soil through vaporization and resuspension followed by dispersion and deposition to off-site locations. The modifications discussed here are designed to provide an estimate of the average contaminant concentrations in the air, ground surface soil, root-zone soil, and surface water of a landscape centered at an off-site distance designated as *OSD* and having units of meters. The off-site landscape at the distance *OSD* is assumed to have the same surface area and landscape properties as the contaminated area.

#### *Atmospheric dispersion modeling*

Substances in outdoor (or ambient) air are dispersed by atmospheric advection and diffusion. Meteorological parameters have an overwhelming influence on the behavior of contaminants in the lower atmosphere. Among them, wind parameters (direction, velocity, and turbulence) and thermal properties (stability) are the most important. The standard models for estimating the time and spatial distribution of point sources of contamination in the atmosphere are the Gaussian statistical solutions of the atmospheric diffusion equation. These models are obtained from solution of the classical differential equation for time-dependent diffusion in three dimensions. The standard Gaussian plume model has the form,

$$C_{\text{air}}(r,y,z) = Q \frac{1}{2 \pi v_w} \times g_1 \times g_2 \quad (62)$$

where  $g_1$  and  $g_2$  represent the respective horizontal and vertical dispersion factors about the plume center line and are given by

$$g_1 = \frac{1}{\sigma_y} \exp \left( - \frac{r^2}{2 \sigma_y^2} \right) \quad (63)$$

$$g_2 = \frac{1}{\sigma_z} \left\{ \exp \left[ - \frac{(z - H)^2}{2 \sigma_z^2} \right] + \exp \left[ - \frac{(z + H)^2}{2 \sigma_z^2} \right] \right\} \quad (64)$$

and where  $C_{\text{air}}$  is the contaminant concentration, in mol/m<sup>3</sup>,  $Q$  is the contaminant source strength, in mole per day;  $r$  is the distance (m) downwind and  $z$  is the distance (m) in air above the source;  $v_w$  is the ground-surface wind speed in m/d,  $H$  is the height of the release, in m; and  $\sigma_z$  and  $\sigma_y$  are, respectively vertical and horizontal dispersion

parameters (m) that increase with increasing distance from the source. However,  $\sigma_z$  can be no greater than  $L(r)$ , the mixing height of the lower troposphere at the distance,  $r$ , from the source.

Detailed solutions for Equations 62 through 64 are widely available and standard models such as SCREEN3 (US EPA, 1995a, 1995b) are also easily obtained from the U.S. Environmental Protection Agency. SCREEN3 provides high-end (i.e. maximum 1-hr, maximum, 1-month, maximum 1-yr concentrations, etc.) solutions for receptor concentrations associated with point, area, and volume sources.

#### *On-site concentration and effective source term*

Contaminant concentration and dispersion in the on-site air-compartment of CalTOX is based on the box-model approach described by Gifford and Hanna (1973). The long-term average pollutant concentration in a region bordered by the CalTOX atmospheric box compartment with volume  $V_a$  and total equivalent pollution sources,  $S'_a$  in mol/d, is given by

$$C_{\text{air}}(\text{box}) = N_a/V_a = \frac{c S'_a}{\text{Area} \times v_w} \quad , \quad (65)$$

where  $c$  is a unitless proportionality constant; *Area* is the area of the region being modeled, and  $v_w$  is the long-term average wind speed in m/d.

In the original Gifford and Hanna (1973) paper,  $c$  ranged from 60 to 600 with a mean around 200 for particles and from 5 to 220 with a mean around 50 for gases. We assume this model to be derived from a mass balance for a box element in the atmosphere such that Gains = Losses.

In the CalTOX system the gains are the total area-based emission rate,  $S'_a$ , (which is equivalent to the source strength  $Q$  used in most atmospheric transport models) and the losses are what is carried out of the volume by an air mass moving at a speed  $v_w$  relative to the land surface so that balancing gains and losses gives,

$$S'_a = C_{\text{air}} \times (\text{height} \times \text{width} \times v_w) / \phi \quad (66)$$

In this expression,  $S'_a$  is the equivalent area emission rate within the box, mol/d;  $C_{\text{air}}$  is the uniform ambient air concentration within the box, mol/m<sup>3</sup>; *height* is the height of the air column at the edge of the box which is the parameter  $d_a$  in CalTOX, m; *width* is the width of the box perpendicular to the effective wind direction and is assumed equal to  $(\text{Area})^{1/2}$ , m;  $v_w$  is the long-term average horizontal wind speed through the box,

$m/d$ ; and  $\phi$  is an adjustment that is assumed to account for the wind direction variability; this factor is greater than one if the wind does not always blow in the same direction. Rearranging Equation 66 gives

$$C_{\text{air}} = \phi S'_a / (\text{height} \times \text{width} \times v_w) \quad (67)$$

substituting  $(\text{Area})^{1/2}$  for *width* and  $d_a$  for *height* gives

$$C_{\text{air}} = \phi S'_a / (d_a \times (\text{Area})^{1/2} \times v_w) \quad (68)$$

comparing this to the box-model equation,  $C_{\text{air}} = (c S'_a) / (\text{Area} \times v_w)$ , implies that

$$c = \phi (\text{Area})^{1/2} / d_a \quad (69)$$

In the Gifford and Hanna (1973), paper, the average urban area was on the order of  $10^9 \text{ m}^2$  so that, with a mixing height of 1000 m, we obtain  $\phi$  in the range 1.6 to 6 corresponding to  $c$  in the range 50 to 200. We select  $\phi = 4.3$  because this value minimizes the discontinuity at the edge of the box when we use the box model for on-site air concentrations and the model for area sources in SCREEN3.

Dividing both sides of Equation 68 by  $S'_a$  and setting  $\phi = 4.3$  gives

$$\chi/Q = \frac{C_{\text{air}}}{S'_a} = \frac{4.3}{\sqrt{\text{Area}} \times v_w \times d_a} \quad (70)$$

As the long-term on-site concentration-to-source ratio. This formulation implies that if we have  $C_{\text{air}}$  in  $\text{mol}/\text{m}^3$  and want to define the equivalent volume source,  $S'_a$  in  $\text{mol}/\text{d}$ , it can be obtained by rearranging Equation 70, and, similarly, if we have  $S'_a$  in  $\text{mol}/\text{d}$  and want to define the equivalent long-term air concentration on-site,  $C_{\text{air}}(\text{box})$  in  $\text{mol}/\text{m}^3$ , it can also be obtained by rearranging Equation 70.

In order to assess the value of the mixing height,  $d_a$ , for use in Equation 70 to characterize volume of air above toxic-substance release site, we use an algorithm published by Hanna et al., (1982). In this scheme, if the land-unit area is greater than or equal to  $6 \times 10^8 \text{ m}^2$ , then the air-compartment mixing depth,  $d_a$ , is 700 m; if the area is less than  $6 \times 10^8 \text{ m}^2$ , then  $d_a$ , is  $0.22 ((\text{Area})^{1/2})^{0.8}$ . For example, in a toxic substances release site area of  $100 \text{ m}^2$ , this would result in a mixing height of 10 m.

Since we use the SCREEN3 model to assess off-site transport, the mixing height for characterizing off-site concentrations relative to the area source of the site, is the SCREEN3 default mixing height for the rural, one-hour maximum concentration at a wind speed of 1 m/s for any given downwind distance.

#### *Determining off-site concentrations*

Off-site  $C_{\text{air}}/S'_a$  ratios are developed by developing a regression algorithm that reproduces the dependence of SCREEN3  $\chi/Q$  ratios for area sources on source area and off-site distance. This process was developed in collaboration with the staff scientists of the California Air Resources Board (ARB). The procedure we developed has the following framework:

- (a) The CalTOX model is used to assess an area source term, that is, the source strength  $Q$  (mol/unit time) of contaminant emanating from a landfill or hazardous waste site. This is the term  $S'_a$  in CalTOX.
- (b) As a basis for estimating off-site air concentrations associated with the gas emissions from a contaminated land unit, we use a model that is provided and approved by the U.S. EPA and widely used by ARB. SCREEN3 (US EPA, 1995a) is the model that meets these requirements and can be used to relate area sources to off-site concentrations in terms of contaminated area and distance from the contaminated area to a receptor.
- (c) SCREEN3 was used to develop a large set of maximum one-hour  $\chi/Q$  ratios associated with a large set of different source areas and different off-site distances.
- (d) From these results, a response surface is developed which allows the mapping of this large set of simulations into an algebraic expression within CalTOX to estimate off-site concentrations.
- (e) An approach described in the SCREEN3 guidance document is used to convert the maximum 1-hour concentration into an annual average off-site concentration.

The SCREEN3 model (EPA, 1995a) was developed to provide an easy -to-use method of obtaining pollutant concentration estimates based on the screening procedures documents issued by EPA (EPA, 1995b). By taking advantage of the rapid growth in the availability and use of personal computers (PCs), the SCREEN3 model makes screening calculations accessible to a wide range of users.

We obtained from U.S. EPA a copy of SCREEN3 and ran simulations for the off-site  $\chi/Q$  ratios from an area source. According to the guidance provided by EPA for using SCREEN3, low-level sources (i.e., sources with stack heights less than about 50m) sometimes produce the highest concentrations during stable atmospheric conditions. Under such conditions, the plume's vertical spread is severely restricted and horizontal

spreading is also reduced. This results in what is called a fanning plume. The recommended calculation procedure (EPA, 1995b) for low-level sources with no plume rise is to find the maximum 1-hour  $\chi u/Q$  using SCREEN3. In the  $\chi u/Q$  term,  $\chi$  is the ground level concentration, mol/m<sup>3</sup>,  $u$  is the 10-m elevation wind speed, m/s, and  $Q$  is the source strength, mol/s. The recommended procedure is different for rural and urban landscapes. For rural cases, F stability is assumed and for urban cases, E-stability is assumed. The maximum 1-hour concentration is computed for a 10-m wind speed of 1 m/s.

In order to develop an algorithm that approximates the behavior of SCREEN3, we ran the area source option to determine the maximum 1-hour concentration associated with rural conditions and a 1 m/s wind speed according to the procedure described above. Urban conditions result in a somewhat lower  $\chi/Q$ . Thus, we elected to use the rural procedure as more appropriate for assessing off-site health effects. We made hundreds of simulations in which we varied the off-site distance, OSD, from 10 to 2000 m. OSD is the distance measured from the edge of the contaminated site. We varied the area of the site (Area) from 100 to 10<sup>6</sup> m<sup>2</sup>. Following the recommendations of the SCREEN3 users manual (EPA, 1995a), we excluded situations in which the off-site distance was shorter than the square-root of the area. Figure 5 below summarizes these results of these simulations and shows how  $\chi/Q$  for the area source varies with OSD and Area.

We next developed an algorithm that provides the best fit of the maximum 1-hour  $\chi/Q$  with  $u = 1$  m/s. We discovered the best fit of this model with the following algorithm

$$\frac{c}{Q}^{hr} = Area^{(-0.28)} \times 10^{-(1.92+0.00057OSD)} + \frac{117.95}{(1.72 \times OSD + \sqrt{Area}) \times [(OSD + \sqrt{Area})^{0.85}]} \quad (71)$$

Relative to the set of estimates for  $\chi/Q$  obtained from SCREEN3, this estimation equation has an  $r^2$  of 0.95, which means that this approximation accounts for 95% of the variance of  $\chi/Q$  generated by SCREEN3 over the same ranges of OSD and Area. The mean value of the ratio of approximated  $\chi/Q$  ratio values to the SCREEN3  $\chi/Q$  values is 1, which means the model fits without bias. The standard deviation of this ratio as applied over the ranges of OSD and Area in Figure 5 is 0.3. This means that 66% of the approximated  $\chi/Q$  values have a residual error of  $\pm 0.3$  or less relative to the SCREEN3 estimated values. Comparison of these approximations relative to the SCREEN3 values are shown in Figure 6.

To obtain concentration estimates for the long-term annual averaging off-site  $\chi/Q$  as needed by CalTOX, we use the EPA (1995b) recommended ratio between a annual maximum concentration and a 1-hour maximum. EPA (1995b) presents ratios for



a "general case" of long-term average and the user is given some flexibility to adjust those ratios to represent more closely any particular application where actual

**X/Q versus distance for an area for nine different area sources**

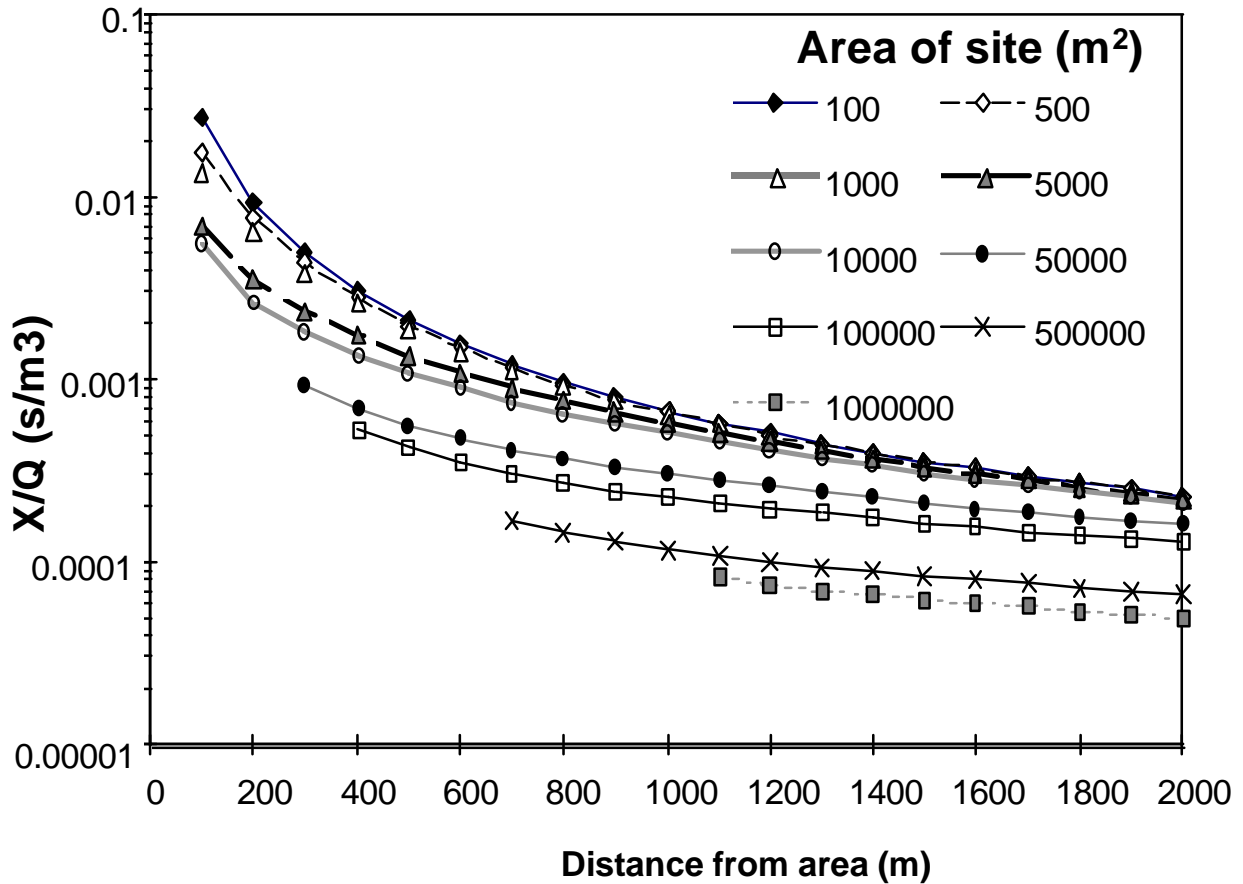


Figure 5. X/Q versus off-site distance (OSD) and contaminated area.

meteorological data are used. To obtain the estimated maximum concentration for an annual averaging time, the EPA recommends multiplying the 1-hour maximum  $\chi/Q$  by 0.08 ( $\pm 0.02$ ). The number in parentheses is the EPA (1995b) recommended limits within which the general ratio may diverge.

Based on these procedures, we determine the annual average off-site air concentrations in CalTOX using the algorithm

$$\frac{c}{Q}^{yr} = 10^{(-1.097 \pm 0.115)} x \{Area^{(-0.28)} \times 10^{-(1.92 + 0.00057 OSD)} + \frac{117.95}{(1.72 \times OSD + \sqrt{Area}) \times [(OSD + \sqrt{Area})^{0.85}]}\} \quad (72)$$

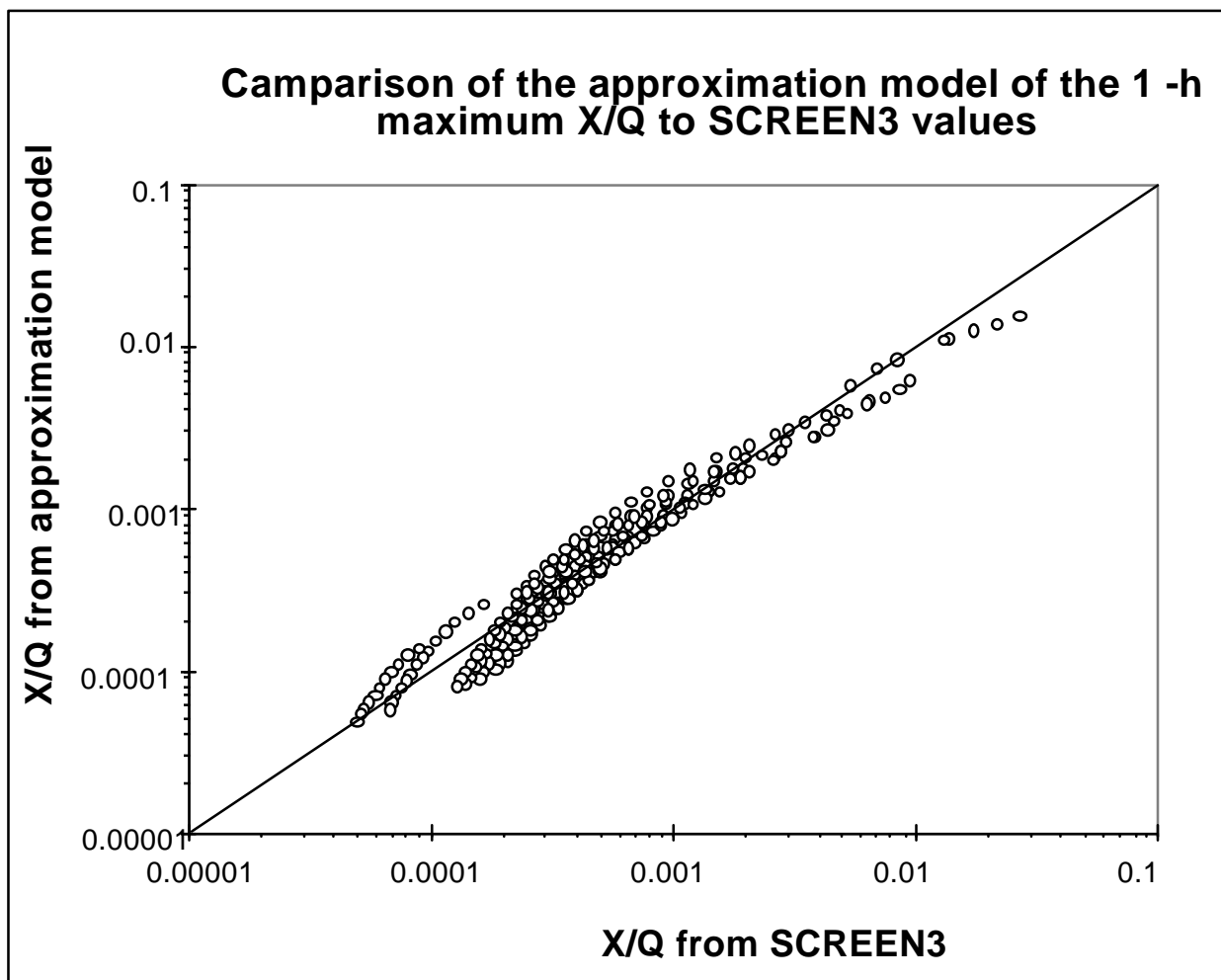


Figure 6. Comparison of CalTOX approximations of X/Q to the SCREEN3 values.

The first term in this Equation 72 is the conversion from the 1 hour maximum  $\chi/Q$  to the annual average  $\chi/Q$  ( $10^{-1.097}$  equals 0.08) and includes the residual error that results from using the approximation equation for the SCREEN3 results. It should be noted that  $\chi/Q$  in equation 72 is equivalent to the ratio  $C_{\text{air}}(\text{off-site})/S'_a$  used in CalTOX.

#### *Calculating off-site surface-media fugacities and concentrations*

The off-site contaminant concentrations in soil layers, vegetation, surface waters and sediment are calculated from Equations 9, 10, and 13 to 17 under steady-state conditions, that is at infinite time; with  $S_g$ ,  $S_s$ , and  $S_w$  set to 0; and with a pseudo source,  $S'_a$ , that would be needed to maintain the off-site air concentration,  $C_{\text{air}}(\text{off-site})$  at the value given in Equation 72 for equivalent on-site concentration,  $Q$  or  $S'_a$ . Thus, a pseudo source is defined as

$$S_a'' = \bar{C}_{air}(OSD) \left( L_a - \frac{T_{pa} T_{ap}}{L_p} - T_{wa} \mathbf{a}_1 \right) \quad (73)$$

This allows the use of a multimedia landscape at the receptor location.

### Contamination of Off-Site Ground Water

In constructing a CalTOX algorithm for off-site transfers in the saturated (ground water) zone we take the perspective that the mathematical formulation does not need to be complex, because, relative to the mathematical algorithm, the greatest degree of uncertainty in applying the model enters through geologic heterogeneity, i.e., the values used for the crucial parameters such as dispersivity. We do not intend that the ground water algorithm developed here for CalTOX should compete with numerical ground water models. Appropriate application of ground water models requires extensive site-specific data. Obtaining this data is time consuming and expensive. Instead we developed a simple model which will account for ground water transport, complete with quantitative uncertainty, so this pathway can be compared with other pathways.

In order to estimate the dilution of contaminants in ground water, we make use of a contaminant plume analysis model described by Domenico and Robbins (1985), which is an extension of an earlier model posed by Domenico and Palciauskas (1982). The latter model has been used by the U.S. EPA (1985) to assess off-site transfers of contaminants at hazardous waste sites. Both of these models have been widely used and cited (see for example Galya, 1987). The model is modified here to include degradation processes in the ground-water zone.

#### *Mathematical development*

Domenico and Robbins (1985) developed an analytical expression for contaminant transport from a finite source in a continuous flow regime. This model has been adapted to solving the problem of the extended pulse approximation to the continuous finite source problem. The dispersion advection equation that applies to the transport of contaminants in an aquifer in the absence of transformation processes has the form

$$\frac{\partial}{\partial t} C_{gw} + v_c \frac{\partial}{\partial x} C_{gw} = D_{lc} \frac{\partial^2}{\partial x^2} C_{gw} + D_{tc} \frac{\partial^2}{\partial y^2} C_{gw} + D_{zc} \frac{\partial^2}{\partial z^2} C_{gw} \quad (74)$$

where  $C_{gw}$  is the contaminant concentration in mass per unit volume of water;  $D_{lc}$  and  $D_{tc}$  are, respectively, the longitudinal and transverse macro-dispersion coefficients for

the contaminant in the aquifer,  $m^2/d$ ; and  $v_c$  is the mean flow velocity of the contaminant in the aquifer,  $m/d$ . As shown in Figure 7, Equation 74 applies to a Cartesian coordinate system in which the ground water and contaminant flow are in the  $x$  direction, the top of the aquifer corresponds to  $z=0$ , and the center of the contaminated site is at  $y=0$ . This equation does not account for the fact that infiltration can cause additional dilution. We elected not to explicitly model this effect, because (1) the effective continuous recharge rates in much of California are quite low and thus it is expected that this effect is not likely to reduce concentrations significantly at the sites we are considering, and (2) ignoring this effect will, at worst, result in a slight overestimate of the ground water concentration and will result in small overestimates of the off-site exposure, which is consistent with the health-protective philosophy of the DTSC with regard to making exposure estimates.

Equation 74 can be modified to account for transformation processes by adding the term  $R_q C_{gw}$ , in which  $R_q$  is the first-order reaction rate constant,  $day^{-1}$ , corresponding to removals by chemical and/or biological degradation processes. As modified, Equation 74 becomes

$$\frac{\partial C_{gw}}{\partial t} + v_c \frac{\partial C_{gw}}{\partial x} + R_q C_{gw} = D_{lc} \frac{\partial^2 C_{gw}}{\partial x^2} + D_{tc} \frac{\partial^2 C_{gw}}{\partial y^2} + D_{zc} \frac{\partial^2 C_{gw}}{\partial z^2} \quad (75)$$

The average contaminant horizontal seepage velocity,  $v_c$ , is derived from the darcy velocity,  $v_{darcy}$ , of ground water in the  $x$  direction using the expression

$$v_c = \frac{v_{darcy}/\beta_q}{1 + 0.001(\rho b_q/\beta_q) K_{dq}} = \frac{v_{darcy}}{\beta_q + 0.001 \rho b_q K_{dq}} \quad (76)$$

where the ratio  $v_{darcy}/\beta_q$  is the ground water pore velocity,  $\beta_q$  is the void fraction in the aquifer zone,  $\rho b_q$  is the bulk density of the aquifer zone,  $kg/m^3$ ; and  $K_{dq}$  is the distribution coefficient in the ground-water zone,  $mol/kg(solid)$  per  $mol/L$  water and 0.001 is the conversion from liter to  $m^3$ .

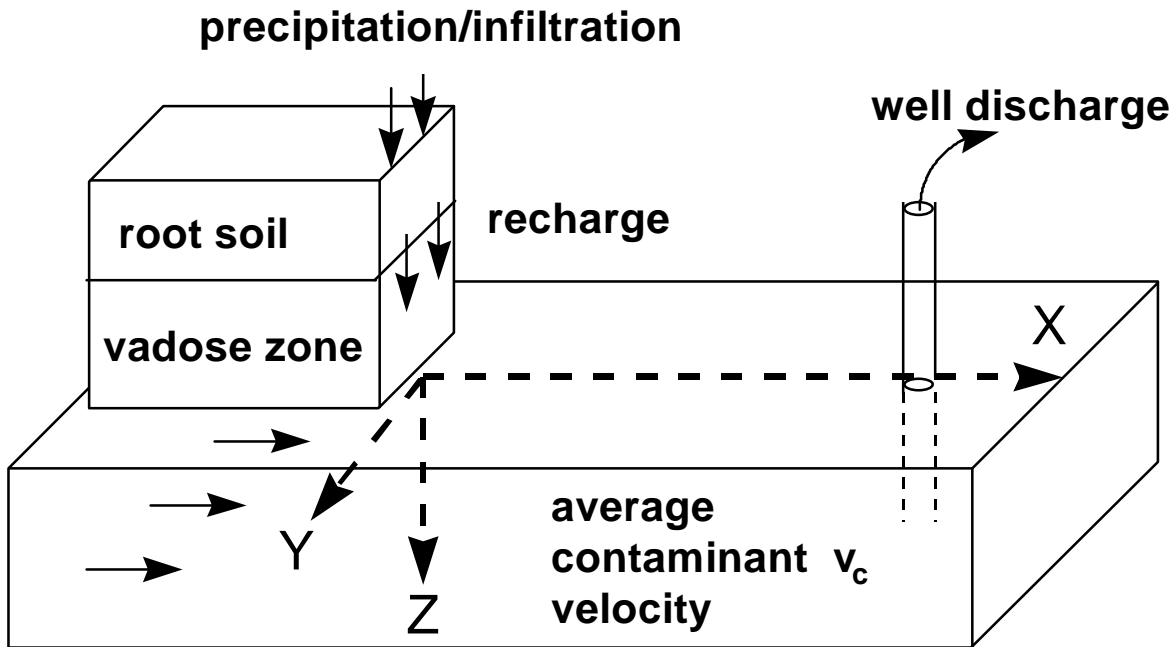


Figure 7. The coordinate system used to assess contaminant transport off site in ground water.

The longitudinal and transverse macro-dispersion coefficients for a contaminant species are calculated from the respective longitudinal and transverse macro-dispersion coefficients,  $D_{lw}$  and  $D_{tw}$ , which are dispersion coefficients for a species transported by water through a porous medium in the absence of adsorption.

$$D_{tc} = \frac{D_{tw}}{1 + 0.001(\rho b_q / \beta_q) K_{dq}} \tag{77}$$

$$D_{lc} = \frac{D_{lw}}{1 + 0.001(\rho b_q / \beta_q) K_{dq}} \tag{78}$$

The dispersion coefficients  $D_{lw}$  and  $D_{tw}$  will depend strongly on the spatial distribution of the pore structure of the porous medium.

For a continuous input of contaminant introduced at concentration  $C_0$  to ground water at  $x=0$  across the width  $Y$  and to a depth  $Z$ , Domenico and Robbins (1985) have shown that the solution to Equation 74 along the contaminant plume centerline is

$$C(x,y,z,t) = C(x,0,0,t) = \frac{C_0}{2} \operatorname{erfc} \left[ \frac{x - v_c t}{2 \sqrt{D_{lc} t}} \right] \times \operatorname{erf} \left[ \frac{Y}{4 \sqrt{D_{tc} x / v_c}} \right] \times \operatorname{erf} \left[ \frac{Z}{4 \sqrt{D_{tc} x / v_c}} \right] \quad (79)$$

Where *erfc* is the complimentary error function and *erf* the standard error function. In addition, Domenico and Robbins (1985) have shown that for a steady state concentration at  $x \ll v_c t$  for  $C_0$  continuous or for the maximum concentration at any point  $x$  along the centerline for a pulse input, Equation 79 becomes

$$C(x,0,0, \text{at } t_{\max}) = C_0 \operatorname{erf} \left[ \frac{Y}{4 \sqrt{D_{tc} x / v_c}} \right] \times \operatorname{erf} \left[ \frac{Z}{4 \sqrt{D_{tc} x / v_c}} \right] . \quad (80)$$

Use of this equation, requires that dispersion in the  $z$  direction be unimpeded. When the contaminant spread is confined within an aquifer of thickness  $d_q$ , then Domenico and Palciauskas (1982) have shown that the appropriate form of Equation 80 is

$$C(x,0,0, \text{at } t_{\max}) = C_0 \operatorname{erf} \left[ \frac{Y}{4 \sqrt{D_{tc} x / v_c}} \right] \times \frac{Z}{d_q} . \quad (81)$$

This solution applies to the situation where there is no chemical or biological decay in ground water. When there is decay the in ground water the attenuation of contaminant concentration to a distance  $x$  off site is given by  $\exp(-R_q x / v_c)$  where  $R_q$  is the first-order removal rate constant in the aquifer and  $x / v_c$  is the time it takes for the contaminant moving in ground water to reach the distance  $x$ . As has been noted by Galya, the theoretical work of Carslaw and Jaeger (1959) demonstrates that the solution of a multidimensional partial differential equation can be formulated by multiplying solutions for the individual dimensions. Therefore, the solution to Equation 75 is simply the solution to 74 multiplied by the time attenuation term. Thus, to convert Equation 81 above to a solution for Equation 75, we simply multiply by  $\exp(-R_q x / v_c)$  giving the more general solution

$$C(x,0,0, \text{at } t_{\max}) = C_0 \operatorname{erf} \left[ \frac{Y}{4 \sqrt{D_{tc} x / v_c}} \right] \times \frac{Z}{d_q} \times \exp(-R_q x / v_c) . \quad (81)$$

This is the formulation used in the revised version of CalTOX. The width of the site,  $Y$ , is estimated as  $\sqrt{\text{Area}}$ .  $Z$  is the on-site penetration depth, which is discussed below.  $C_0$  is the average concentration in the on-site ground water over the exposure duration, ED. This expression is set equal to  $C_{gw}$ , which is derived below. Equation 81 translates this into the average concentration that would pass through an aquifer at a distance  $x$  from

the boundary of the site. It should be noted, however, that this concentration would not begin to pass the point  $x$  until the time,  $x/v_c$ .

*On-site ground water concentration and the penetration depth, Z*

As the ground water in the aquifer passes below the contaminated vadose zone soil, the contaminated water of the vadose soil will leach into the moving ground-water stream as a result of recharge advection. The depth of penetration of the contaminant depends on the horizontal velocity of the ground water, the transverse dispersion coefficient in the aquifer and the longitudinal path taken by ground water under the contaminated site. These processes are illustrated in Figure 8. Domenico and Palciauskas (1982) have shown that the penetration depth,  $Z$ , at the contaminated site boundary depends on plume spreading by recharge advection and by dispersion. We assume that the contaminant concentration within the ground water penetration zone is diluted relative to concentration in vadose-zone water by the velocity of the water relative to the effective penetration velocity of the contaminant. In the CalTOX model, recharge is used to define mass input to the aquifer. This mass balance requires that if the penetration depth,  $Z$ , represents the depth to which the vadose-zone water penetrates at its concentration,  $C_{vw}$ , then  $Z$  must make balance the expression

$$C_{vw} \times recharge \times Area = Z \times C_{gw} \times v_c \times \sqrt{Area} \quad (82)$$

where  $C_{vw}$  is contaminant concentration in the water of the vadose zone, mol/m<sup>3</sup>;  $C_{gw}$  is the contaminant concentration in the water ground-water zone within the penetration depth  $Z$ , mol/m<sup>3</sup>; *recharge* is average ground-water recharge at the site, m/d; and  $\sqrt{Area}$  is the assumed longitudinal dimension of the site. Domenico and Palciauskas (1982) have estimated  $Z$  to be given by

$$Z = \sqrt{D_{tc}t_c} \quad (83)$$

However, in applying this estimate of Z, we restrict Z to be less than or equal to the aquifer depth  $d_q$ .  $D_{tc}$  is the transverse dispersivity of the contaminant and  $t_c$  is the time it takes ground water to flow horizontally under the site and is given by

$$t_c = \frac{\sqrt{\text{Area}}}{v_c} \tag{84}$$

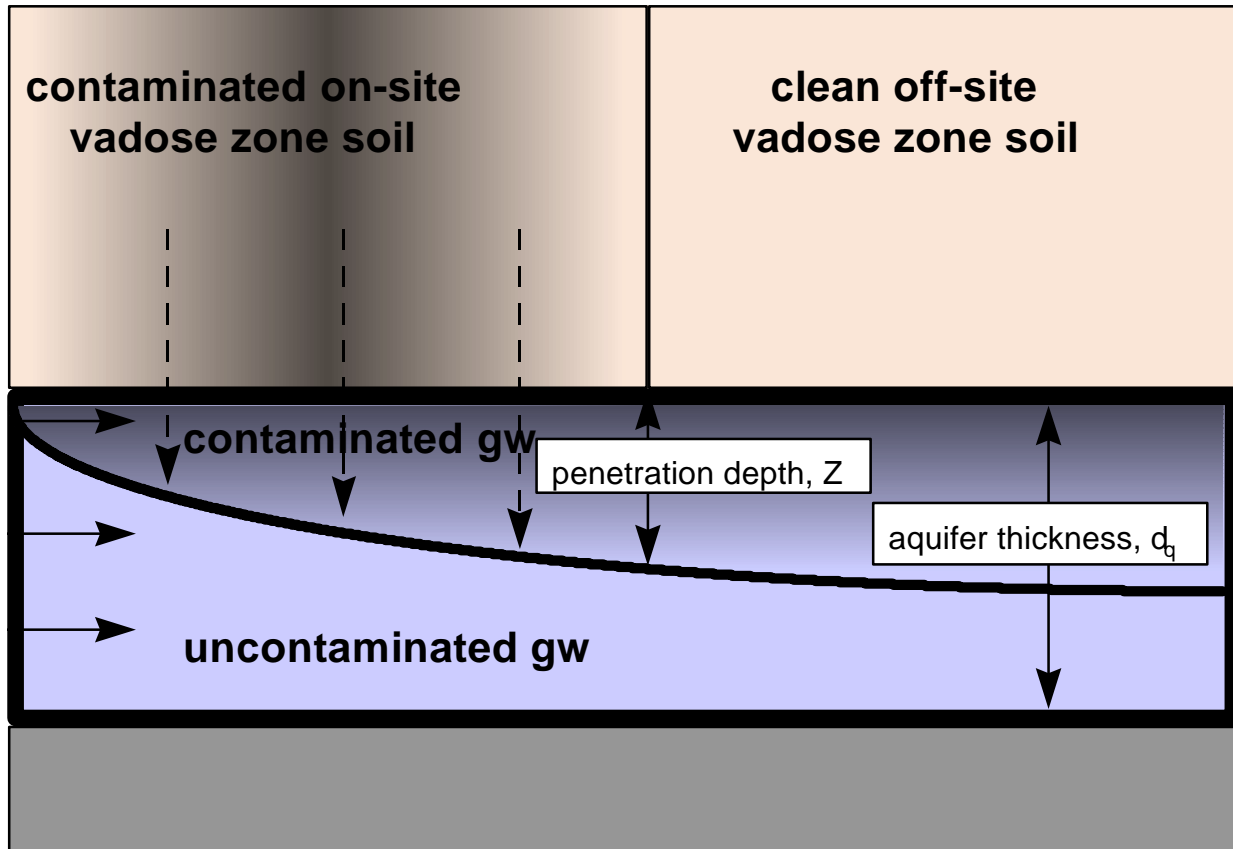


Figure 8. An illustration of the model used to assess the penetration depth of contaminated water from vadose soil into the moving ground-water in the aquifer.

By combining Equations 82 through 84, we obtain a conservative screening estimate of the concentration of contaminant in ground-water below the site within the aquifer depth,  $d_q$  as

$$C_{gw} = \frac{C_{vw} \times recharge \times \sqrt{\text{Area}}}{v_c \times Z} \tag{85}$$



## SUMMARY AND DISCUSSION

This report describes four major additions or modifications that were made to the CalTOX model during 1995 and 1996 in order to address some of the limitations that were identified in the early version of the model. These changes include (1) redefining the CalTOX equations so that there can be both batch and continuous inputs to the root-zone soil, (2) altering the way the plants compartment interacts with soil and air, (3) allowing CalTOX to handle chemical concentrations in soil that exceed the aqueous-phase solubility limit, and (4) adding to CalTOX the ability to simulate off-site transfers of contaminants through air pathways and through the subsurface environment—vapor phase-transport in the vadose zone and ground water transport. These modifications were carried out to make CalTOX more useful, in part to apply to the process of waste classification at hazardous-waste landfills.

In order to make the CalTOX model more applicable to a broader range of environmental problems, it has been modified so that batch inputs, continuous inputs or zero inputs can be specified for the root-soil zone. In addition, the CalTOX model has been modified so that rather than specifying the time-dependent compartment fugacities, concentrations, and inventories at specific times, these state variables are now reported as the average value over an exposure duration, ED. This allows for better use of the model for comparisons. Nevertheless, CalTOX still provides a table listing the time history of the root-soil, vadose-zone, and ground-water compartment inventories as well as the time history of annual daily intake.

In order to improve the reliability of the plant/air/soil interaction model in CalTOX and to bring it into consistency with the recent work of Paterson et al. (1994), several modifications were made. In CalTOX 2.3, the above ground vegetation is modeled as interacting with the soil solution and with the air compartment. The interaction of above-ground plant tissues (primarily leaves) with the root-soil compartment is by root uptake and translocation through the transpiration stream going up the xylem tubes and the transport of nutrients (sugars) down the phloem tubes. The interaction of plants with the air compartment is by diffusion of gas-phase contaminants through the stomata, diffusion of gas-phase contaminants through the cuticle tissue as a result of partitioning from air, and the accumulation and diffusion of solid-phase contaminant that has been deposited on leaf surfaces. The portion of vegetation below the ground surface has now been added as a separate phase to the root-soil compartment. This change was made to reflect the large exchange surface that root tissues have with soil and soil solution.

The CalTOX model has been modified so that it can handle "large" masses (high concentrations) of chemical in the two soil compartments. The earlier version was limited to compartment masses (low concentrations) which did not exceed the limits of solubility in the soil-water. The soil water solubility limit defines the soil fugacity limit. To achieve this, CalTOX was modified so that mass transfer at concentrations that

exceed the soil fugacity limit can be simulated. The modification was applied to the root-zone soil compartment, but also impacts the vadose-zone soil compartment. The modification to CalTOX allows any contaminant in the root zone to exist as a distributed non-aqueous-phase mass NAPM. The contaminant NAPM behaves as a separate phase, not in the water, air or particles of soil, that exists as a reservoir of specified mass that can maintain the soil compartment at saturation fugacity until the NAPM is depleted. After the NAPM is depleted, the transport and transformation of a chemical in soil layers is simulated according to the first order kinetics that are used in the earlier versions of the CalTOX model under the assumption of no NAPM phase. It should be noted that these modifications to CalTOX allow the treatment of distributed, non-moving NAPM. The equations do not treat non-aqueous phase liquid (NAPL) flow.

A new algorithm has been added to CalTOX to provide an estimate of the average contaminant concentrations in the air, ground surface soil, root-zone soil, and surface water of a landscape centered at an off-site distance designated as  $OSD$  and having units of meters. These are the off-site concentrations that are attributable to air dispersion from the toxic-substances release site. Off-site concentration-to-source ratios,  $C_{air}/S'_a$ , are developed by constructing a regression algorithm that reproduces the dependence of model generated values of this ratio for area sources on source area and off-site distance. The EPA SCREEN3 model was used to develop this fitting algorithm. This process was developed in collaboration with the staff scientists of the California Air Resources Board (ARB). The CalTOX off-site air concentration algorithm has an  $r^2$  of 0.95 relative to SCREEN3, which means that this approximation accounts for 95% of the variance of the  $C_{air}/S'_a$  ratios generated by SCREEN3 over the same ranges of off-site distance and Area. We find that 66% of the approximated  $C_{air}/S'_a$  values have a residual error of  $\pm 0.3$  or less relative to the SCREEN3 estimated values.

In constructing a CalTOX algorithm for off-site transfers in the saturated (ground water) zone we take the perspective that the mathematical formulation does not need to be complex, because, relative to the mathematical algorithm, the greatest degree of uncertainty in applying the model enters through geologic heterogeneity, i.e., the values used for the crucial parameters such as dispersivity. We do not intend that the ground water algorithm developed here for CalTOX should compete with numerical ground water models. Appropriate application of ground water models requires extensive site-specific data. Obtaining this data is time consuming and expensive. Instead we developed a simple model which will account for ground water transport, complete with quantitative uncertainty, so this pathway can be compared with other pathways.

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